FLUORESCENCE OF THE URANYL SALTS

BY

EDWARD L. NICHOLS AND HORACE L. HOWES

IN COLLABORATION WITH

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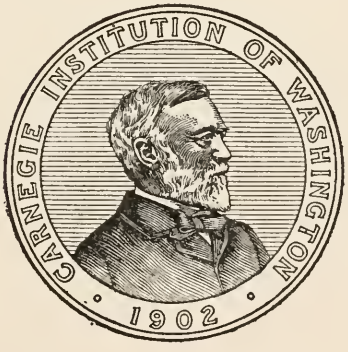

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PREFACE.

This volume, the completion of which has been much delayed by the participation of America in the World War, contains the results of an investigation covering a period of eight years. The discovery by Becquerel and Onnes, that the fluorescence of certain uranyl compounds is resolved into groups of narrow line-like bands when these substances are excited to luminescence at very low temperatures, suggested to the present authors the desirability of a thorough and systematic study of this subject.

The spectra of numerous uranyl salts, many of which were especially prepared for this purpose, have now been mapped. Owing to the extraordinarily complex character of the phenomena, no satisfactory theory has as yet been evolved, but the mass of facts here recorded and the general principles established will, it is hoped, afford a basis for the successful theoretical development of this important and little understood branch of the science of radiation.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
May 24, 1919.

FLUORESCENCE OF THE URANYL SALTS.

By Edward L. Nichols and Horace L. Howes.

I. HISTORICAL INTRODUCTION.

The beginnings of precise knowledge concerning the luminescence of the compounds of uranium are to be found in the classical memoirs of George Gabriel Stokes and of Alexandre Edmond Becquerel. It is true that Brewster[1], who observed the fluorescence of chlorophyl and other substances in 1833 and gave the phenomenon the name of *internal dispersion*, mentioned a yellow glass, doubtless the "canary glass" of commerce, which exhibited the same property, but it remained for Stokes,[2] by means of the beautiful experiments described in his papers entitled "The Change in the Refrangibility of Light," to really elucidate the phenomena and to lay the foundation for all subsequent work on fluorescence.

Having observed, by the use of suitable light-filters and by his ingenious and elegant method of transverse dispersion, the unusual character of the fluorescence and absorption of this glass, Stokes proceeded to the investigation of such compounds of uranium as he was able to procure. From the nitrate he made the acetate, oxalate, and phosphate; also uranates of potassium and calcium and the oxides. He also obtained specimens of autunite (uranyl calcium phosphate) and chalcolite (uranyl copper phosphate). After observations of these minerals he writes (Sec. 145):

"The intervals between the absorption bands of green uranite were nearly equal to the intervals between the bright bands of which the derived spectrum (*i. e.*, the fluorescence spectrum) consisted in the case of yellow uranite. *After having seen both systems I could not fail to be impressed with the conviction of a most intimate connection between the causes of the two phenomena, unconnected as at first sight they might appear. The more I examined the compounds of uranium, the more this conviction was strengthened in my mind.*"

Upon reading Stokes's memoir one can not but feel that had he had at his command a modern spectroscope he would infallibly have anticipated by more than half a century much of the recent work on fluorescence. He used light-filters to prevent the exciting beam from submerging the fluorescence on the one hand and to exclude the exciting

[1] Sir David Brewster, Trans. Roy. Soc. Edin., vol. xii. 1833.
[2] Stokes, Phil. Trans., 1852, p. 463; 1853, p. 385.

rays from entering the eye on the other, and thus by means of a prism held to the eye was able to observe the spectra of both fluorescence and absorption with surprising accuracy.

Paragraph 148 of his paper describes his observations on uranyl nitrate. In the following quotation of that paragraph certain passages forecast in an extraordinary manner some of the conclusions reached in subsequent chapters of the present monograph:

"The sun's light was reflected horizontally by a mirror and condensed by passing through a large lens. It was then transmitted through a vessel with parallel sides containing a moderately strong ammoniacal solution of a salt of copper. The strength of the solution and the length of the path of the light within it were such as to allow of the transmission of a little green besides the blue and violet.

"A crystal of nitrate of uranium was then attached to a narrow slit and placed in the blue beam which had been transmitted through the solution, the crystal being turned toward the incident light. The light coming from the crystal through the slit was then viewed from behind and analyzed by a prism. A most remarkable spectrum was then exhibited, consisting from end to end of nothing but bands arranged at regular intervals. The interval between consecutive bands appeared to increase gradually from the red to the violet, just as is the case with bands of interference. Although this interval appeared to alter continuously from one end of the spectrum to the other, the entire system of bands was made up of two distinct systems, different in appearance and very different in nature. The less refrangible part of the spectrum, where, only for the crystal, there would have been nothing but darkness, was filled with narrow bright bands due to the light that had changed its refrangibility. The more refrangible part of the spectrum was occupied by the system of bands of absorption. The interval between the most refrangible light band and the least refrangible dark band of absorption appeared to be a very little greater than one band interval, so that had there been one more band of either kind the least refrangible absorption band would have been situated immediately above the most refrangible bright band. With strong light I think I have seen an additional band of this nature."

Becquerel, in the course of his work on phosphorescence, notes the fact that most of the compounds of uranium show a strong emission of light when examined with the phosphoroscope. He determined the duration as three to four thousandths of a second; and to test his empirical formulæ made measurements of the rate of decay which, as will be seen, are in good agreement with the results described in Chapter IV of the present treatise. With a prism of carbon bisulphide he observed 8 bright bands in the spectrum of the phosphorescent light of uranyl nitrate; he determined the approximate range in the violet and ultra-violet of the exciting rays; noted that the bands in the spectra of various uranyl salts, such as the chloride, fluoride, and uranyl potassium sulphate, occupy different places. He also estimated their relative displacements when compared with the bands of the nitrate. By comparing the spectrum of the nitrate during excita-

tion with that of the afterglow, Becquerel reached the very important conclusion that the fluorescence and phosphorescence are identical. This point finds ample confirmation in the present work.

In 1872, E. Becquerel returned to the study of the uranyl salts. The following are the conclusions reached in this investigation:[1]

(1) The salts of the protoxide of uranium are inactive.
(2) Many, but not all, salts of the sesquioxide (uranyl salts) are active.
(3) Five, six, and sometimes seven bright bands, or groups, are visible; lying between the Fraunhofer lines C and F.
(4) The positions of the bands vary for different salts, but are always the same for a given salt.
(5) The acid of composition determines the disposition of both bright and dark bands.
(6) In double salts of the same acid the composition of individual groups is the same, but their position is not the same for the different salts.
(7) In a given substance the distance between bands, as viewed in the spectroscope, increases from red to violet; but the differences of wave-length decrease. The ratio of the above distances to the square of the mean wave-length is nearly constant throughout the spectrum, and this ratio $(d/2)$ is the same for the various salts.
(8) No simple relation is apparent between the location of homologous bands in different compounds and the chemical properties of the compounds.
(9) The absorption spectra also differ for the various compounds and the absorption bands seem to form a continuation of the fluorescence series.
(10) The location and character of these spectra being fixed and definite for each compound, we have the basis for an analytical method similar to but less general than ordinary spectrum analysis.

In 1873, Henry Morton and H. Carrington Bolton published an account of extended studies of the fluorescence and absorption of the uranyl salts.[2] Their list contains 85 substances, chiefly of *their* own preparation, including 17 double acetates; but not all of these compounds were found to be fluorescent. Readings were made on the Bunsen scale in vogue at that time, and some of these, for comparison with our own determinations, will be found, reduced to approximate wave-lengths, in Chapter III.

Figure 1, which is reproduced from the paper of Morton and Bolton, gives an excellent general view of some of the most interesting of their observations. The unshaded portions are fluorescence bands, the shaded regions are the bands of absorption. The partial resolution of the bands in several cases is clearly shown and the breaking-up into distinct groups of the uranyl ammonium chloride; also the coincidence in certain cases of absorption and fluorescence in what in this monograph we shall term the reversing region.

[1] E. Becquerel, Comptes Rendus, LXXV, p. 296. 1872.
[2] Morton and Bolton, Chem. News, pp. 47, 113, 164, 273, 244, 257, 268. 1873.

The authors note specifically the following further important characteristics of the spectra of the uranyl salts:

(1) The steeper gradation of light on the side toward the violet in the case of bands showing a single crest.
(2) The weakness of the outer bands, both toward red and violet, compared with the central bands of the spectrum.
(3) The overlap of fluorescence and absorption.
(4) The systematic shift of bands when a salt is dissolved in water and other solvents.
(5) The remarkable changes due to the dehydration of salts containing water of crystallization.
(6) The effects of heating.

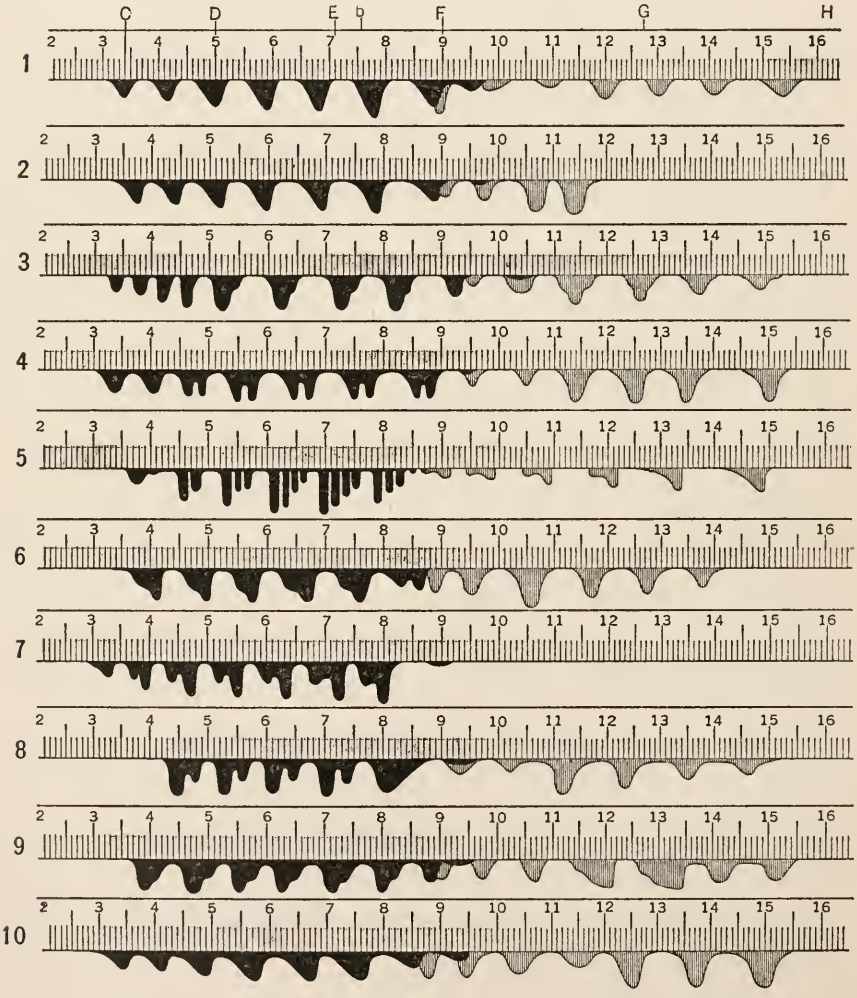

FIG. 1.—1. Uranic nitrate. 2. Uranic acetate. 3. Sodio-uranic acetate. 4. Uranic oxychloride (acid), mixed hydrates. 5. Potassio-uranic oxychloride. 6. Uranic oxyfluoride. 7. Bario-uranic oxyfluoride. 8. Uranic phosphate, mixed hydrates. 9. Calcio-uranic phosphate. 10. Ammonio-uranic sulphate.

Morton and Bolton, like Becquerel, refer to the possibility of determining the composition of uranyl compounds from the observation of their fluorescence spectra and state that even minute quantities, present as impurities, may be detected by means of their characteristic bands.

Hagenbach[1] likewise published a considerable list of fluorescence bands for the uranyl salts, but his paper adds little to the data of Becquerel and of Morton and Bolton.

In 1903, J. Becquerel and Onnes, working in the cryogenic laboratory at Leyden, excited various uranyl salts to fluorescence at the temperatures of liquid air and of liquid hydrogen respectively.

At −185° C. each band of the spectrum was found to be resolved into a group of much narrower bands. The spectra of a number of compounds were photographed, using a grating spectrograph, and the most prominent bands were mapped.

It was shown in the course of this investigation that the resolved spectra are made up of series of bands, the frequency interval varying slightly for different compounds; also that each group in a given spectrum is similar to all the other groups as regards the arrangement and the relative intensities of its components. In the *reversing region*, where fluorescence goes over into absorption, the coincidence in position of bright and dark bands was pointed out. Further cooling to the temperature of liquid hydrogen rendered the individual bands sharper and more line-like, but there was no further resolution.

This resolution of the fluorescence spectra by cooling constitutes the most important advance subsequent to the discoveries of Stokes and of E. Becquerel, since it affords a means of studying the more intimate structure of these remarkable spectra. It forms, indeed, the starting-point for the present investigation.

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[1] Hagenbach, Annalen der Physik., v. 146, p. 395. 1872.

II. THE STRUCTURE OF FLUORESCENCE SPECTRA.

A fluorescence spectrum consists of one or more bright bands, and these may greatly vary in width, from the very broad bands, filling a great part of the visible spectrum, characteristic of the fluorescent dyestuffs and the phosphorescent sulphides, to the line-like bands of the ruby.

Such a spectrum is either a *homogeneous complex* of systematically related components or a heterogeneous complex of unrelated components. In either case the components frequently overlap, giving the appearance of a single band, which may be described as a *mixed band* (an unresolved heterogeneous complex) or a *homogeneous band*, respectively. Where the components overlap less completely or not at all the appearance is that of a group of bands.

It is probable that a heterogeneous complex is always the result of a mixture of two or more compounds the fluorescence of each of which by itself gives a homogeneous complex.

The phosphorescent sulphides afford spectra which may serve to illustrate the above classification. A strontium sulphide with bismuth as the active metal and a flux of sodium sulphate, for example, has a fluorescence spectrum which appears to the eye to consist of a single band with its crest at 0.480 μ. A recent spectrophotometric exploration by Dr. H. L. Howes,[1] however, shows a group of closely over-lapping components (see fig. 2). The crests of these are located as shown in table 1; and as they are systematically related, forming members of a series having a uniform interval of frequency difference, this is to be regarded as a homogeneous band or homogeneous complex.

FIG. 2.

Similarly, the fluorescence of a barium sulphide with copper as the active metal and a flux of sodium borate, when viewed through an

[1] Proceedings American Philosophical Society, LVI, p. 258. 1917.

ordinary spectroscope, has a spectrum which seems to consist of a single very broad band. A spectrophotometric study reveals, however, two neighboring and overlapping bands. These have their crests in the red and green respectively and are complex. (See fig. 3.)

TABLE 1.—*Approximate wave-lengths of visible crests in the spectrum of a phosphorescent strontium sulphide* (Sr; Bi; Na_2SO), *No. 13.*

μ.	Visible crests $1/\mu \times 10^3$.	Intervals.	μ.	Visible crests $1/\mu \times 10^3$.	Intervals.
0.4430	2257	58	0.5238	1909	
.4547	2199	58	.....	.....	2×58
.4670	2141	58	.5562	1793	.....
.4801	2083	58	.....	.....	2×58
.4938	2025	.....	.5921	1677	.....
.....	.....	2×58			

The components of the band in the green are members of a series having a constant frequency interval of 70 (see table 2), while the components of the band in the red form a series with an interval of

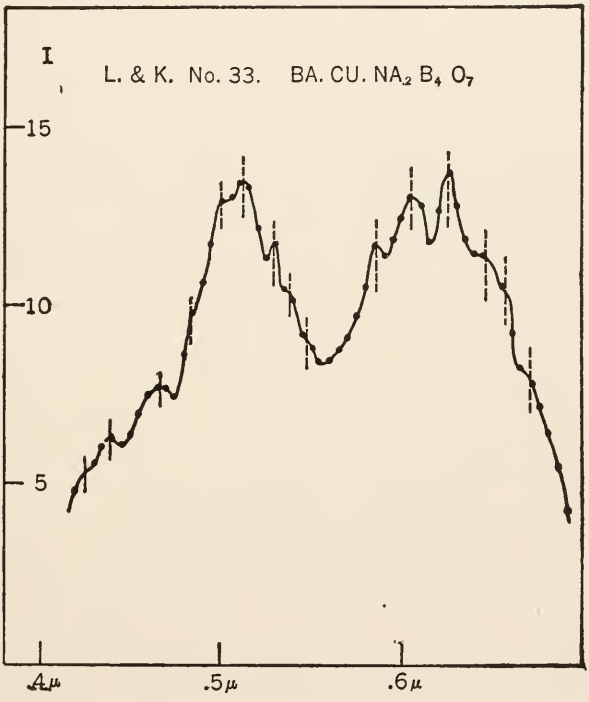

FIG. 3.

26.6. The two series overlap, as may be seen from figure 3. In this example the spectrum as a whole forms a heterogeneous complex made up of two homogeneous complex bands which are partially superimposed.

The fluorescence spectrum of commercial anthracene affords an example of a heterogeneous complex easily resolved into a group of

bands. There are at least 7 such bands, 4 of which are seen in the spectroscope with a region in the violet not readily resolved by visual observations. This violet fluorescence has, however, been determined photographically by Miss McDowell.[1] The approximate location of the bands in this spectrum is shown in figure 4.

TABLE 2.—*Approximate wave-lengths and frequencies of visible crests in the spectrum of a phosphorescent barium sulphide* (Ba; Cu; $Na_2B_4O_7$).

Green complex.		Red complex.	
Visible crests. μ.	Intervals. $1/\mu \times 10^3$.	Visible crests. μ.	Intervals. $1/\mu \times 10^3$.
0.4255	70	0.5000	.....
.4386	.....	.....	26.6×2
.....	70×2	.5136	.....
.4673	70	.....	26.6×2
.4831	70	.5283	.....
.5000	.....	.....	26.6×7
.....	70×2	.5861	.....
.5376	.....	.....	26.6×2
		.6049	.....
		.....	26.6×2
		.6250	.....
		.....	26.6×2
		.6465	26.6
		.6578	.....
		.6695	26.6

While all of these bands are present in the fluorescence of the impure commercial product, they are not all due to any one constituent. By solution and subsequent fractional sublimation, as is well known, it is possible to partially separate the substance into pure anthracene, which has a violet fluorescence and a residue containing chrysogen, the fluorescence of which is green.

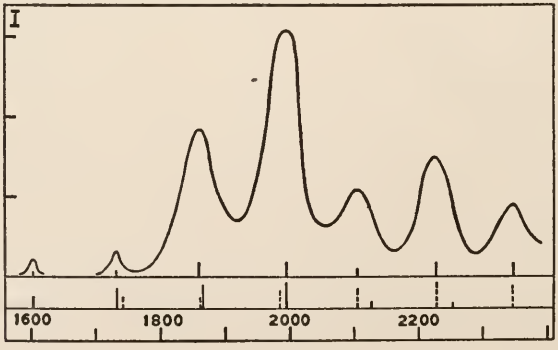

FIG. 4.

Miss McDowell has shown that the bands 6, 7, and 8 belong to the anthracene thus obtained, while band 4 is also present in its spectrum. Bands 1, 2, 3, and 4 are characteristic of the green residue.

[1] Miss L. S. McDowell, Physical Review (1), XXVI, p. 155. 1908.

The presence of band 4 in both spectra may be due to the imperfect separation of the two substances. That it is much stronger in spectra obtained from mixtures showing green fluorescence than from those the fluorescence of which is blue-violet would seem to warrant ascribing it to the chrysogen component, a conclusion strengthened by the consideration of the placing of the bands. The most probable positions of the crests are given in table 3. The positions of the three bands assigned to anthracene are from photographic measurements by Miss McDowell;[1] those due to chrysogen are from spectrophotometric readings made in 1910,[2] combined with more recent observations.

TABLE 3.—*Wave-lengths and frequencies of the bands of commercial anthracene.*

Band.	μ.	$1/\mu \times 10^3$.	Difference.
1.....	0.6235	1603	130
2.....	.5790	1733	127
3. Chrysogen...	.5362	1860	136
4.....	.5005	1996	.....
5.....	.4750	2105	122
6. Anthracene...	.4490	2227	120
7.....	.4260	2347	.....

It will be noted that the three bands in the blue-violet are members of a series having a frequency interval of about 121; also that the 4 bands of greater wave-length form a series with a somewhat greater interval, *i. e.*, about 131. Band 4 is too near to band 5 to belong to the anthracence series, but may, within the rather large errors due to the breadth and vagueness of these bands, be regarded as one of the chrysogen series.

There are several criteria based on experimentally established facts by which the homogeneity or heterogeneity of a fluorescence band or complex may be determined.

CRITERIA OF HOMOGENEITY.

(1) The position and distribution of intensities in a homogeneous band is independent of the mode of excitation. This was established by various observations published several years ago,[3] and subsequent experience strengthens our conviction that it is a general principle and that shifts in position and change of form are to be regarded as indications of heterogeneity due to the presence of more than one luminescent substance.

(2) The distribution of intensities in a homogeneous band is such that the curve has a single well-marked maximum. The slope toward the violet is steeper than that toward the red, like that in the corresponding curve of intensities of an incandescent black body.

[1] Miss L. S. McDowell, l. c.

[2] Nichols, E. L., Proc. Am. Philos. Soc., XLIX, p. 277.

[3] See Nichols and Merritt, Studies in Luminescence, Carnegie [Inst. Wash. Pub. No. 152, pp. 24, 38, 144.

In the case of a partially resolved or wholly resolved homogeneous complex the envelope obtained by drawing a curve through the crests of the group of bands has the above form, as has the curve of intensities of each of the component bands.

A departure from this type indicates heterogeneity. Thus, for example, the curve in figure 2 suggests a partially resolved homogeneous complex, while that in figure 3 indicates a heterogeneous complex or mixed band.

The best examples thus far are found among the uranyl salts. Figure 5 shows á typical case in which the envelope of the 7 bands of a uranyl salt is shown and with an enlarged scale of wave-lengths the distribution of intensities of a single band of the same spectrum. Other illustrations will be found in subsequent chapters of this monograph.

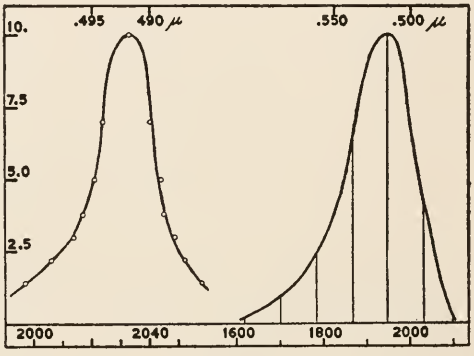

FIG. 5.

(3) In a homogeneous complex, the fluorescence spectrum is identical with that observed during phosphorescence as regards the position, relative intensity, and structure of its component bands. Nor is there any change in these respects during the process of decay. Change of color in passing from the fluorescent to the phosphorescent stage or during phosphorescence is therefore a criterion of heterogeneity, since such changes are due to the presence of bands having different rates of decay.

Such subjective changes of color as are due to the loss of intensity during decay are excluded from the above statement.

Most of the phosphorescent sulphides afford examples of heterogeneity clearly indicated by the above criterion and confirmed in other ways, while the spectra of the uranyl salts, in spite of their great complexity, are found, from this criterion, too, strictly homogeneous.

(4) .Persistence of color and of structure when excited to fluorescence at different temperatures, the different components of the spectrum suffering the same relative changes of intensity, may be regarded as a criterion of homogeneity, but the complex changes of structure revealed by the resolution of spectra in the process of cooling to the temperature of liquid air do not necessarily indicate heterogeneity.

As will be shown in subsequent chapters, the fluorescent spectra of the uranyl salts, for example, are profoundly modified by the cooling of the substance, and yet these spectra conform to all other known criteria of homogeneity.

III. PRELIMINARY OBSERVATIONS ON CERTAIN URANYL SALTS.[1]

Because of their brilliant luminescence and the interesting character of their spectra of fluorescence and absorption, the uranyl compounds have been the subject of extended study. A brief account of the work of previous observers in this field has been given in Chapter I.

Our original purpose in taking up the study of these substances was to determine whether the different bands of the fluorescence spectrum are to be regarded as independent, each with its own region of excitation, or whether they form a homogeneous complex, such that the excitation of one necessarily involves the excitation of all. In this inquiry we have been led to the investigation of many other questions.

Since, as was first shown by Becquerel and Onnes[2] in the paper cited in Chapter I, the bands of the uranyl salts are resolved into groups of narrow components by cooling, it is at the temperature of liquid air and chiefly by photographic methods that the intimate structure of the fluorescence and absorption spectra is to be determined. The study of the spectra at ordinary temperatures, however, is not without significance.

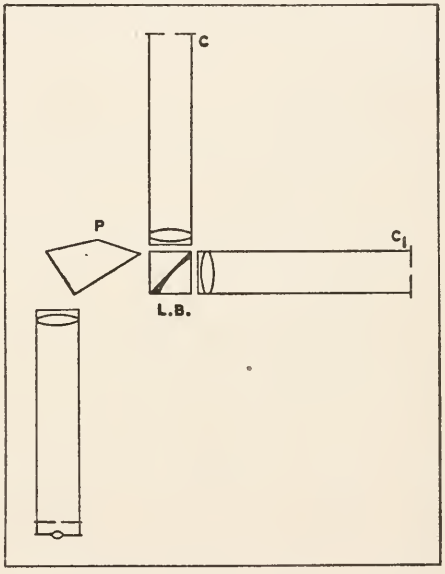

FIG. 6.

In this work, where the width of the bands is from 50 to 100 Å. U., the spectrophotometer is indispensable. Many of the measurements to be described were made with a special instrument which combines the features of the constant deviation spectrometer and the Lummer-Brodhun spectrophotometer. It is essentially a spectrometer of the Hilger type, with two collimators C and C' (fig. 6), a Lummer-Brodhun cube $L.B.$, and a constant-deviation prism P with carefully calibrated drum.

[1] Certain of the observations contained in this chapter have been published in the Physical Review (1), XXXIII, p. 355, but many of the data there given have been replaced by more complete investigations kindly done at our request by Dr. Frances G. Wick (Physical Review (2), v. 11, p. 121. Feb. 1918.

[2] Becquerel and Onnes, Leiden Communications, 110. 1909.

For the determination of wave-lengths the eyepiece is provided with a pointer in the focal plane and also with the usual slides for isolating the region under observation.

The collimator slits have micrometric adjustment, and to provide for convenient comparison through the very great range of intensities occurring in the study of fluorescence, the illumination of the comparison slit can be varied by moving the comparison light along a photometer bar to any desired distance from the slit. The observing telescope can be replaced by a camera whenever photographs of the spectra are desired. With this instrument the wave-lengths of the bands could be determined by setting the pointer to the region of greatest brightness as estimated by the eye and the relative intensities could be measured spectrophometrically.

Tables 4 to 10 contain the resulting data for several salts; also the frequencies corresponding to the wave-lengths and frequency intervals. The measurements and computations were kindly made by Miss Wick, who likewise determined the relative brightness of the bands in several of the spectra.

From the data in these tables some of the salient features of the uranyl spectra may be deduced, viz:

(1) The weakest bands are at the ends of the spectrum, *i. e.*, in the red and the blue.

(2) The brightest band is not in the center, being third from the violet end and sixth from the red end when all 8 bands of the spectrum are visible.

(3) Taking the frequency intervals, instead of the differences of wave-length, the bands, with the exception of the band of shortest wave-length (band 8), are equidistant, at least within the rather large

TABLE 4.—*Fluorescence bands of the nitrates.*

Uranyl nitrate (Anhydrous); ($UO_2(NO_3)_2$). Width of bands about 70 Å. U.				Uranyl nitrate (tri-hydrate) ($UO_2(NO_3)_2+3H_2O$). Observations on a single large crystal; width of bands about 100 Å. U.				Uranyl nitrate (hexahydrate) ($UO_2(NO_3)_2+6H_2O$).		
Position of crest of band.	$1/\mu\times10^3$.	Interval.	Intensity.	Position of crest of band.	$1/\mu\times10^3$.	Interval.	Intensity.	Position of crest of band.	$1/\mu\times10^3$.	Interval.
4720.0	2118.6			4871.0	2052.9		49.2	4720.8	2118.2	
		65.8				84.3				69.8
4871.2	2052.8		50.2	5079.7	1968.6		100.0	4881.8	2048.4	
		88.2				86.8				86.4
5090.0	1964.6		100.0	5314.0	1881.8		64.5	5096.3	1962.0	
		87.6				87.6				86.1
5327.6	1877.0		52.7	5573.4	1794.2		20.0	5330.6	1875.9	
		87.4				87.4				87.3
5587.6	1789.6		25.1	5859.0	1706.8			5591.2	1788.6	
		87.2				84.6				87.2
5874.0	1702.4			6164.3	1622.2			5877.5	1701.4	
		84.7								85.0
6181.2	1617.7							6186.5	1616.4	

TABLE 5.—*Fluorescence bands of the double nitrates.*

Ammonium uranyl nitrate (β), $UO_2(NO_3)_2 \cdot NH_4NO_3$. (Accuracy of setting not to be expected; the double crest (*a* and *b*) of each band is flat of nearly equal intensity, rather broad, and not well separated.)				Potassium uranyl nitrate, $UO_2(NO_3)_2 \cdot KNO_3$. (Bands broad and fuzzy; over 100 units wide; crests distinctly double, with a third crest toward the violet.)			
Position of crest of band.	$1/\mu + 10^3$.	Interval.		Position of crest of band.	$1/\mu \times 10^3$.	Interval.	
		a–*a*	*b*–*b*			*a*–*a*.	*b*–*b*.
a–4639.6	2155.3	.....	.....	*a*–4696.0	2129.5	.....	.....
b–4705.3	2125.0	.....	.....			71.9	.....
		72.0	59.6	*a*–4860.0	2057.6	.....	.....
a–4800.0	2083.3	.....	.....	*b*–4904.0	2039.0	.....	.....
b–4841.6	2065.4	.....	.....			88.2	81.5
		80.3	84.6	*a*–5077.5	1969.4	.....	.....
a–4992.6	2003.0	.....	.....	*b*–5108.3	1957.5	.....	.....
b–5048.3	1980.8	.....	.....			83.7	87.3
		88.8	87.2	*a*–5303.5	1885.5	.....	.....
a–5224.0	1914.2	.....	.....	*b*–5347.0	1870.2	.....	.....
b–5280.6	1893.6	.....	.....			85.7	86.7
		87.1	87.1	*a*–5556.0	1799.8	.....	.....
a–5473.0	1827.1	.....	.....	*b*–5607.3	1783.5	.....	.....
b–5535.6	1806.5	.....	.....			86.5	86.2
		87.6	90.0	*a*–5836.5	1713.3	.....	.....
a–5748.7	1739.5	.....	.....	*b*–5891.5	1697.3	.....	.....
b–5825.6	1716.5	.....	.....			86.3	86.7
		80.2	85.5	*a*–6146.3	1627.0	.....	.....
a–6026.6	1659.3	.....	.....	*b*–6209.0	1610.6	.....	.....
b–6130.8	1631.0	.....	.....				

TABLE 5.—continued.

Rubidium uranyl nitrate, $UO_2(NO_3)_2 \cdot RbNO_3$. (Bands very broad with two poorly defined crests. With less excitation the bands appear single. Settings are only roughly approximate.)				
Position of crest of band.	$1/\mu \times 10^3$.	Internal.		Intensity.
		a–*a*.	*b*–*b*.	*b*–*b*.
b–4828.0	2071.0	.....	.....	.....
			89.0	68.3
a–4994.5	2002.2	.....	.....	.....
b–5045.5	1982.0	.....	.....	.....
		83.0	83.0	100.0
a–5210.7	1919.2	.....	.....	.....
b–5265.3	1899.0	.....	.....	.....
		85.9	89.0	39.4
a–5454.5	1833.3	.....	.....	.....
b–5525.0	1810.0	.....	.....	.....
		90.7	92.0	7.6
a–5738.8	1742.6	.....	.....	.....
b–5820.5	1718.0	.....	.....	.....
		79.6	84.0	2.1
a–6012.0	1663.0	.....	.....	.....
b–6119.0	1634.0	.....	.....	.....

TABLE 6.—*Fluorescence bands of the sulphate.*

Uranyl sulphate ($UO_2SO_4 + 3H_2O$).					
Position of crest of band.	$1/\mu \times 10^3$.	Interval.		Intensity.	
		a–*a*.	*b*–*b*.	*a*.	*b*.
a–.....	.....	.....	.....	.....	.....
b–0.4753	2103.9	.....	.....	.....	.....
		.....	80.0	.....	.....
a– .4886	2041.7	.....	.....	.....	.....
b– .4941	2023.9	.....	.....	.....	.....
		85.7	85.2	27.97	38.72
a– .5099	1961.0	.....	.....	.....	.....
b– .5158	1938.7	.....	.....	.....	.....
		86.6	85.8	91.79	100.00
a– .5335	1874.4	.....	.....	.....	.....
b– .5397	1852.9	.....	.....	.....	.....
		86.1	86.7	50.04	53.79
a– .5592	1788.3	.....	.....	.....	.....
b– .5662	1766.2	.....	.....	.....	.....
		86.8	88.9	19.27	20.14
a– .5877	1701.5	.....	.....	.....	.....
b– .5962	1677.3	.....	.....	.....	.....
		84.2	87.1	.....	.....
a– .6183	1617.3	.....	.....	.....	.....
b– .6284	1590.2	.....	.....	.....	.....

uncertainties inevitable in the attempt to locate the crests of such broad bands. Of this band, which occupies the region lying, roughly, between 0.4650 μ and 0.4750 μ, only the less-refrangible edge is seen, the other side being more or less cut off by absorption. Its apparent distance from band 7 is thus reduced.

(4) In some cases there is sufficient evidence of resolution to enable the location of two or more crests. Further evidences of complexity will be found in the spectrophotometric study of these spectra, to be considered in a subsequent paragraph.

TABLE 7.—*Fluorescence bands of the double sulphates.*

Sodium uranyl sulphate ($UO_2SO_4.Na_2SO_4$).			
Position of crest of band.	$1/\mu\times10^3$.	Interval.	Intensity.
4744.0	2107.9		.....
		71.3	
4910.0	2036.6		27.29
		85.6	
5125.0	1951.0		100.00
		83.4	
5354.2	1867.6		46.77
		84.6	
5608.4	1783.0		15.13
		85.4	
5890.5	1697.6		5.88
		84.8	
6200.2	1612.8		.....

Potassium uranyl sulphate ($UO_2SO_4.K_2SO_4$).			
Position of crest of band.	$1/\mu\times10^3$.	Interval.	Intensity.
4778.0	2093.0		.....
		66.9	
4935.5	2026.1		35.33
		78.1	
5133.6	1948.0		100.00
		84.3	
5365.6	1863.7		41.22
		84.2	
5619.2	1779.5		12.85
		85.2	
5902.9	1694.3		.....
		81.7	
6201.2	1612.6		.....

Ammonium uranyl sulphate ($UO_2SO_4.(NH_4)_2SO_4$). (The two crests of each band very close and narrow.)				
Position of crest of band.	$1/\mu\times10^3$.	Interval.		Intensity.
		a–a.	*b–b.*	
a–4929.0	2028.8			25.5
b–4950.0	2020.2			.....
		83.6	84.0	
a–5140.8	1945.2			100.00
b–5164.8	1936.2			.....
		84.6	84.2	
a–5374.5	1860.6			21.43
b–5399.5	1852.0			.....
		83.6	84.5	
a–5627.0	1777.0			11.86
b–5657.8	1767.5			.....
		84.0	82.7	
a–5906.5	1693.0			.....
b–5935.5	1684.8			.....
		83.7	85.2	
a–6213.7	1609.3			.....
b–6251.4	1599.6			.....

Rubidium uranyl sulphate ($UO_2SO_4.Rb_2SO_4$).			
Position of crest of band.	$1/\mu\times10^3$.	Interval.	Intensity.
4757.0	2102.2		.....
		73.9	
4930.0	2028.3		38.52
		80.9	
5136.0	1947.4		100.00
		84.8	
5368.7	1862.6		49.35
		83.2	
5619.8	1779.4		19.77
		82.8	
5894.0	1696.6		.....
		82.5	
6195.5	1614.1		.....

TABLE 7.—*Fluorescence bands of the double sulphates*—continued.

Uranyl cæsium sulphate ($UO_2SO_4.CsSO_4$). (Bands over 100 units wide with sharp maxima near the end toward red and secondary maxima (bracketed) much less bright and sharp toward the violet.)			
Wave-length of crest of band.	$1/\mu \times 10^3$.	Interval.	Intensity.
4702.0	2126.7		.....
		75.8	
4876.0	2050.9		50.49
(4933.0)		85.7	
5088.5	1965.2		100.00
(5151.5)		84.4	
5317.0	1880.8		53.09
(5338.0)		86.6	
5573.5	1794.2		16.90
(5670.0)		85.4	
5852.0	1708.8		6.36
		86.8	
6165.0	1622.0		.....

TABLE 8.—*Fluorescence bands of two acetates.*

Uranyl acetate.			
Position of crest of band.	$1/\mu \times 10^3$.	Interval.	Intensity.
4710.0	2123.0		.....
		73.0	
4878.0	2050.0		48.16
		86.9	
5094.0	1963.1		100.00
		86.2	
5328.0	1876.9		48.86
		86.7	
5586.0	1790.2		22.36
		86.4	
5869.2	1703.8		.....
		86.3	
6182.3	1617.5		.....

Ammonium uranyl acetate.				
Position of crest of band.	$1/\mu \times 10^3$.	Interval.		Intensity.
		a–*a*.	*b*–*b*.	
b–4680.0	2136.0			.....
		.....	88.6	
a–4804.5	2081.3			.....
b–4884.3	2047.4			61.42
		87.8	84.5	
a–5016.3	1993.5			.....
b–5094.6	1962.9			100.00
		86.0	87.0	
a–5242.2	1907.5			.....
b–5330.8	1875.9			46.12
		85.3	84.2	
a–5487.8	1822.2			.....
b–5581.0	1791.7			18.40
		.....	88.3	
a–.....	.....			.....
b–5870.6	1703.4			.....
		.....	92.5	.....
a–.....	.....			.....
b–6207.5	1610.9			.....

RELATIVE INTENSITIES OF THE BANDS.

To indicate graphically the relative intensities of the bands, we may plot their strength, expressed in terms of energy, as ordinates and wave-lengths of the crests as abscissæ.

The resulting curve (see figs. 7, 8, 9, and 10) is a sort of envelope for the entire spectrum corresponding to the curve of distribution of energy. It resembles in type the curve of energy found in the case of the broad, single-banded fluorescence described in earlier communications,[1] being single-crested and steeper toward the violet. As has been pointed out in Chapter II, these curves are very similar to the energy curve for temperature radiation.

Figure 7 contains the envelopes thus plotted of 5 uranyl double sulphates. Of these, 4 have their crests at approximately the same wave-length (0.515 μ). Curve E (cæsium uranyl sulphate) is shifted slightly, an effect due to the presence of a strong component of each band on the violet side of the main crest which influences the estimates

[1] Nichols and Merritt, Physical Review (1), XVIII, p. 403; XIX, p. 18.

TABLE 9.—*Fluorescence bands of two phosphates.*

Uranyl phosphate ($H \cdot UO_2 \cdot PO_4$). (Bands narrow and distinct.)			Ammonium uranyl phosphate ($H_2(NH_4)_2UO_2(PO_4)_2$). (Bands very distinct with narrow crests.)		
Position of crest of band.	$1/\mu \times 10^3$.	Interval.	Position of crest of band.	$1/\mu \times 10^3$.	Interval.
4847.0	2063.0		4845.0	2063.9	
		71.7			69.7
5020.3	1991.9		5014.6	1994.2	
		83.8			82.7
5240.7	1908.1		5231.3	1911.5	
		83.7			83.2
5481.1	1824.4		5469.6	1828.3	
		84.9			83.7
5748.6	1739.5		5730.8	1744.6	
		82.9			83.8
6036.5	1656.6		6021.0	1660.8	
					82.5
			6336.0	1578.3	

TABLE 10.—*Fluorescence bands of a nitrate, oxalate, and fluoride.*

Uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$).			Uranyl oxalate $UO_2C_2O_4 \cdot 3H_2O$.			Potassium uranyl fluoride ($UO_2\ F_2 \cdot 2KF$).		
Position of crest of band.	$1/\mu \times 10^3$.	Interval.	Position of crest of band.	$1/\mu \times 10^3$.	Interval.	Position of crest of band.	$1/\mu \times 10^3$.	Interval.
4700.0	2127.6		4715.0	2120.9				
		72.1			75.1			
4865.0	2055.5		4888.0	2045.8		4803.2	2081.9	
		89.3			92.3			79.8
5085.8	1966.2		5119.0	1953.5		4994.8	2002.1	
		86.6			86.3			86.8
5320.0	1879.6		5355.0	1867.2		5219.5	1915.3	
		88.3			86.9			85.6
5582.3	1791.3		5617.0	1780.3		5465.2	1829.7	
		87.0			88.2			89.1
5867.0	1704.3		5910.0	1692.1		5745.0	1740.6	
		86.2			88.2			89.1
6179.8	1618.1		6235.0	1603.9		6055.0	1651.5	

of the location of the latter. The envelopes of the 4 nitrates in figure 8 have the same characteristics. The crests of 3 agree (at 0.510 μ), while the envelope *D* of rubidium uranyl nitrate, in the spectrum of which the bands are vaguely double-crested, is displaced. In the two uranyl acetates (fig. 9) the same identity of type and position shows itself.

To reduce these spectrophotometric measurements to relative energy units the distribution curve of the comparison light must be known. This curve for the acetylene flame, which was the source employed, has been carefully determined, and data published by Coblentz were used in the computation.

In certain cases the resolution of the bands is such that the brightness of two crests can be determined and two overlapping envelopes drawn, as in figure 10, which pertains to the spectrum of $UO_2SO_4+3H_2O$. The relative brightness of the two crests is seen to vary slightly from band to band.

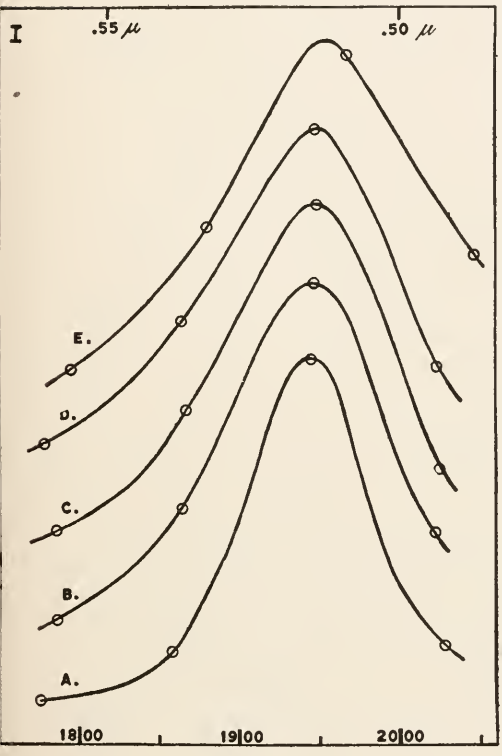

FIG. 7.

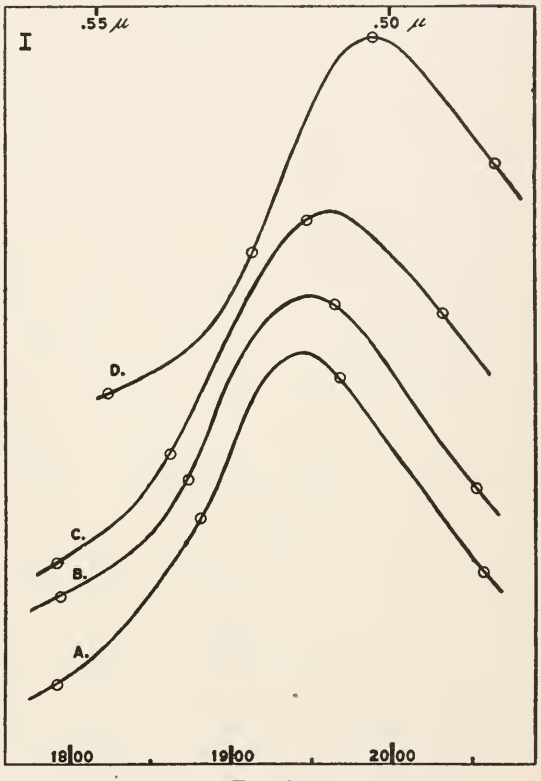

FIG. 8.

The changes in the position of the crests in the case of the sulphates, nitrates, and acetates is illustrated in figure 11, in which a typical curve from each family of salts is given.

While these measurements by Dr. Wick do not include all the spectra for which such determinations are possible, they suffice to demonstrate the essential uniformity of type of the envelopes and to show that within a given family, such as the double sulphates or the nitrates, the crests occupy the same region in the spectrum. It will be seen, when we come to the consideration of the detailed structure of these fluorescence spectra, that there is a slight but definite shift of all the bands with molecular weight.

Spectrophotometric measurements of single unresolved bands, practicable with accuracy only in the case of some of the brightest, show the

curve of distribution to be of the same type as that obtained when the envelope is drawn for the entire spectrum, *i. e.*, the type associated with what we have termed a simple band. (See *A* in fig. 5, Chapter II, which is the energy curve for the brightest band of uranyl potassium sul-

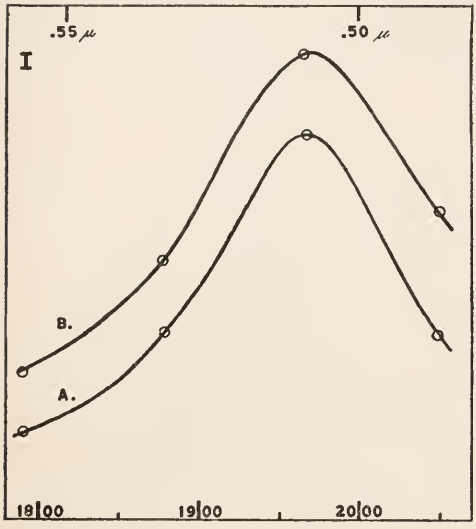

Fig. 9.

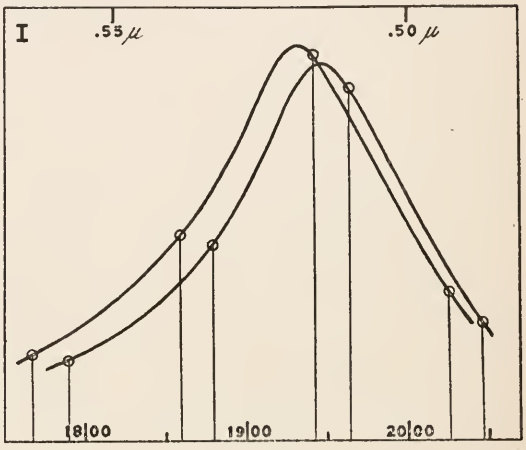

Fig. 10.

phate with the scale of wave-lengths, adjusted so as to make the width nearly the same as that of the envelope (*B*) for the same substance.)

The most striking feature distinguishing these spectra from one another to the eye, excepting where partial resolution occurs, is the varying width and sharpness of the bands.

With the spectrophotometer it is possible to obtain a more definite expression of this feature, as may be seen from figures 12 and 13, in which are depicted, from such measurements, the three brightest bands of uranyl nitrate (crystallized) and uranyl potassium sulphate. It will be noted that the bands overlap at the base, but to a greater extent in the nitrate than in the potassium sulphate, where the bands are narrower and more sharply defined.

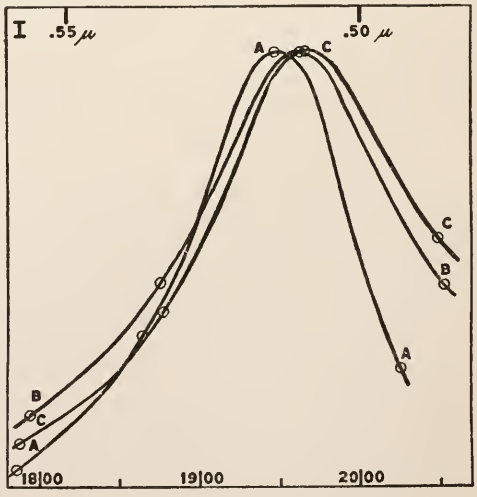

Fig. 11.

A more detailed use of the instrument, working with narrow slits and making settings at closer intervals, will often bring out the complexity of single bands, where the overlapping of the components is such as to conceal the structure Figures 14, 15, 16, and 17 give the results of such a study by Miss Wick. The existence of numerous partly sub-

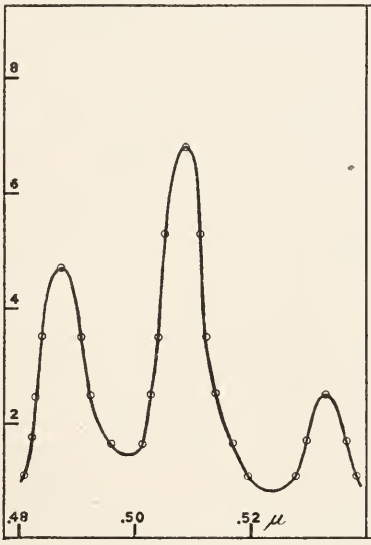

Fig. 12.

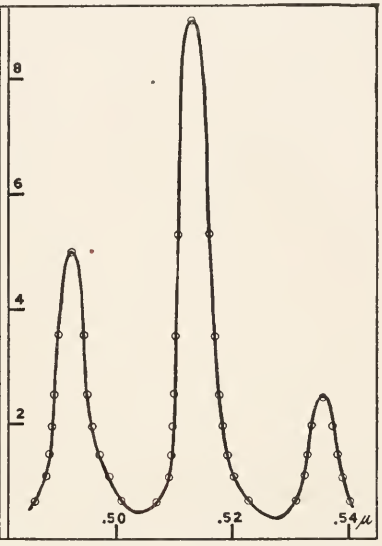

Fig. 13.

Showing the relative intensities of the brightest fluorescence bands of uranyl nitrate (fig. 13) and uranyl potassium sulphate (fig. 14).

merged crests is apparent in the curves, corresponding to the complexity of structure which these bands show when the substance is excited at the temperature of liquid air. The vertical lines indicate the position of the bands, as observed at low temperatures by methods to be described in subsequent chapters.

That these lines in general do not coincide with the positions of the crests might seem to indicate that there is no definite relation between the spectra at the two temperatures or that the accuracy of the curves is in doubt; but the discrepancies are quite in accordance with the results obtained by the detailed study of the spectra of the double chlorides (Chapter V), where the spectra are sufficiently resolved at +20° C. to enable us to trace the changes on cooling, measure the definite shifts, and discover the remarkable mechanism of the process of resolution.

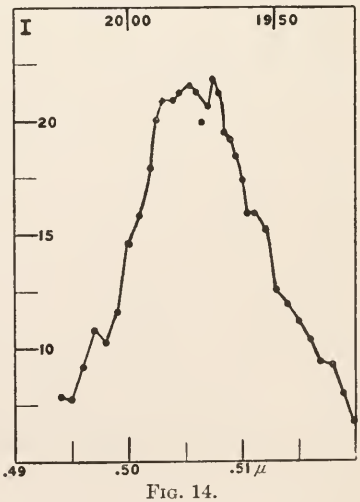

Fig. 14.

EXCITATION BY LIGHT OF DIFFERENT WAVE-LENGTHS.

If all the bands of the luminescence spectrum are due to the vibrations of a single connected system it would be natural to expect that an agency which excited one would also excite the rest, especially if luminescence is due to the recombination of ions dissociated by the exciting light, or to the return of an electron set free by the exciting

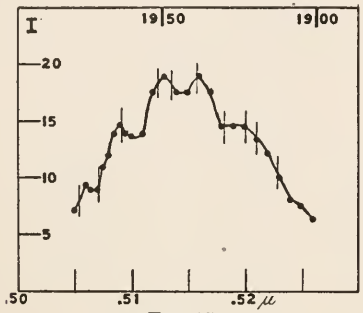

Fig. 15.

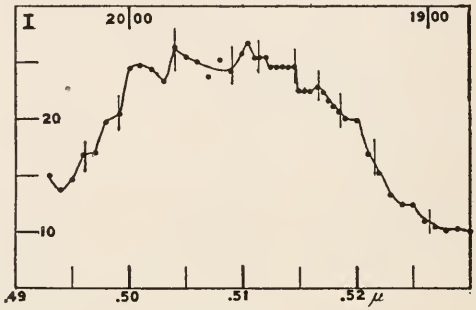

Fig. 16.

agency. On the other hand, if each band is dne to some process going on in one particular compound or molecular aggregation, wave-lengths might be found which would excite one band and not the rest, or which would at any rate excite the bands in different degree.

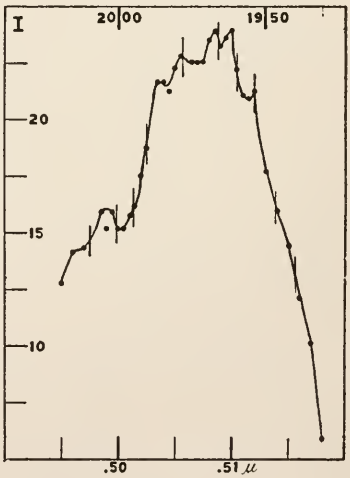

Fig. 17.

To test this matter we have measured the distribution of intensity in the bands for excitation by different lines in the ultra-violet spectrum of the quartz mercury lamp. The intensity of fluorescence with this excitation is not sufficient to permit the measurement of all the bands, so that the three brightest bands only have been measured. In table 11 the intensities for excitation by the different lines in the mercury spectrum are given for five different uranyl salts. Curves showing the variation of the relative intensity with the wave-length of the exciting light are shown for uranyl-nitrate crystals in figure 18, and for the double sulphate in figure 19. In each case the intensity of the most intense band has been put equal to 10. The variation was greater in the case of the double sulphate than in the case of any other salt studied. The observations were repeated in the case of this substance on two different days and a comparison of the full and dotted

curves indicates the extent to which the results agree. In the case of the other salts studied, curves very similar to that of figure 18 were obtained.

TABLE 11.—*Relative intensity of excitation of the three brightest bands by five different lines in the spectrum of the mercury arc.*

	Wave-length of exciting light.	Intensity[1] of luminescence at crest.			Ratio *a/b.*	Ratio *c/b.*
		Band *a.*	Band *b.*	Band *c.*		
Uranyl-potassium sulphate:	0.436μ	12.5	22.7	7.45	0.55	0.33
	.407	12.6	26.4	8.45	.48	.32
Band *a*.....4,920	.366	10.5	23.2	6.65	.45	.29
b.....5,130	.313	16.25	22.9	8.27	.71	.36
c.....5,360	.254	8.83	13.9	4.25	.64	.31
Uranyl phosphate:	.436μ	10.0	10.2	3.07	.98	.30
	.407	6.04	6.06	1.90	1.00	.31
Band *a*.....5,015	.366	9.7	9.7	2.47	1.00	.25
b.....5,239	.313	11.1	10.4	3.04	1.07	.29
c.....5,483	.254	6.85	5.35	.....	1.28	.....
Uranyl nitrate (anhydrous):	.436μ	22.9	38.7	15.5	.59	.41
	.407	15.3	22.7	9.30	.67	.41
Band *a*.....4,849	.366	15.3	20.7	8.87	.47	.43
b.....5,071	.313	21.8	31.6	11.7	.69	.37
c.....5,311	.254	6.0	7.7	3.2	.78	.42
Uranyl nitrate (crystals):	.436μ	18.6	27.2	10.0	.69	.37
	.407	17.5	24.5	8.6	.73	.35
Band *a*.....4,869	.366	12.2	18.3	7.5	.67	.41
b.....5,086	.313	17.3	25.6	9.6	.67	.38
c.....5,329	.254	8.3	10.5	4.0	.79	.38
Uranyl fluorid fluor-ammonium:	.436μ	10.3	11.2	3.7	.92	.33
	.407	23.3	25.0	7.7	.93	.37
Band *a*.....5,008	.366	20.4	25.7	7.6	.79	.30
b.....5,237	.313	37.5	43.4	11.5	.87	.27
c.....5,460	.254	15.8	17.6	5.7	.90	.32

[1]The intensities given in table 11 are not corrected for energy distribution in the acetylene flame.

It will be noticed that the lower curve in figures 18 and 19 indicates a very nearly constant ratio between the intensity of the brightest band and that of the band lying next in the direction of the red. But if we compare the brightest band with the band lying next to the violet side we find a considerable variation in the ratio of intensities, especially in the case of the double sulphate. It appears to us probable that this variation is the result of a partial absorption of the luminescence by the substance. The absorbing power of a given salt differs for the different mercury lines used, so that in some cases the exciting light may penetrate much further into the substance than in others. It is clear that those bands for which the absorption is greatest will appear relatively weaker when the exciting light penetrates a considerable distance into the substance, even if the relative intensity of the excitation of the different bands is really the same for all wave-lengths of the exciting

light. The observed distribution of energy would correspond with the actual distribution only in case an excessively thin layer of the substance is excited—so thin that the absorption of the light emitted is negligible. As a matter of fact, the band lying to the violet side of the maximum is in a region where the absorption is considerable, while the brightest band and those lying to the red are in the region where the absorption is small. The constancy of the ratio in the case of the lower curves, and the small variation of the ratio shown by the upper curves, are therefore entirely consistent with the view that the observed variations are the result of absorption, and that the first effect of excitation, whatever may be the wave-length of the exciting light, is to produce all of the bands with a definite and constant intensity distribution.

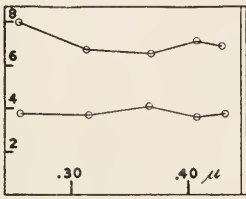

FIG. 18.

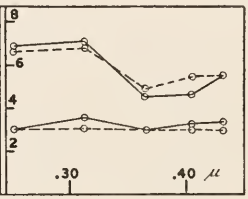

FIG. 19.

Relative intensities of the brightest fluorescence bands of uranyl nitrate (fig. 18) and uranyl-potassium sulphate (fig. 19). The intensity of the brightest band is put equal to 10. The upper curve in each figure refers to the band lying next to the brightest toward the violet. The lower curve refers to the band toward the red. Abscissæ give the wave-length of the exciting light. (See table 11.)

The observations recorded in the foregoing paragraphs all tend to indicate that the fluorescence spectrum of a uranyl salt is a homogeneous complex.

The envelope is single-crested and has the form typical of a simple band. Neither its position nor form is modified by changing the mode of excitation. To test this conclusion we have made many experiments under widely varying conditions, especially in the way of selective and monochromatic excitation of the resolved spectra, where it should be possible to observe critically the disappearance or enhancement of single narrow components of groups of series.

The remarkable effects of selective excitation recorded by Wood in the case of fluorescent vapors might lead to the expectation of similar or analogous changes in the uranyl spectra. All these attempts have thus far been without result, and we are inclined, therefore, to regard the spectrum as a unit and to consider it as a broad, simple band, which unlike the other bands of this type as yet discovered, consists of resolved instead of completely overlapping components.

Studies to be described in Chapter IV are in confirmation of this view in that the criterion for a simple band, based upon the phenomena of phosphorescence, is fulfilled.

THE ABSORPTION SPECTRUM AT ORDINARY TEMPERATURES.

The resemblance of the absorption spectra of the uranyl salts to their fluorescence spectra, which is so striking as to have led both E. and H. Becquerel to regard the absorption series as a continuation of the series of fluorescence bands, can be fully investigated only by observations at low temperatures. Since the absorption extends into the ultra-violet, moreover, photographic methods are necessary. The study of the absorption at ordinary temperatures is, however, not without significance, and the use of the spectrophotometer in this work brings out certain features not easily discernible in the photographic plates.

The salts thus studied by us were in powdered form and the location, relative intensity, and character of the bands lying within the visible spectrum were determined by measuring the intensity of the light transmitted by an extremely thin layer between glass plates, or in some instances by observing the spectrum of white light reflected from the surface of the powder. Recourse to the latter method is, indeed, frequently necessary because of the great and rapidly increasing opacity of these substances in the blue and violet.

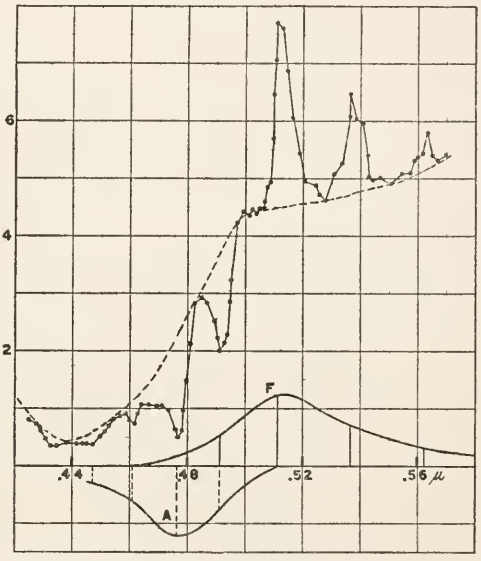

FIG. 20.—Transmission of a thin layer of uranyl-potassium sulphate, showing absorption bands and three of the fluorescence bands. Curves *F* and *A* show the relative intensities of the bands of fluorescence and absorption respectively.

The nature of the results of such measurements is sufficiently shown in figure 20, which is plotted from determinations of the light transmitted by a thin layer of uranyl potassium sulphate. The source of light was an acetylene flame.

The measurements cover not only a considerable portion of the absorbing region, but also a part of the region containing the fluorescence bands. Three of these bands show very clearly, even when superposed upon the brilliant continuous spectrum of the acetylene flame. The absorption begins a little on the violet side of the brightest luminescence band and extends into the ultra-violet. It will be noticed that there are several definite and narrow absorption bands, which appear to be superposed upon a broad band, or region, of general absorption. This appearance of a broad band might result from the overlapping of the group of narrow absorption bands, only the crests of which can be observed. In estimating the relative intensity of the

absorption bands we have adopted the first view and have assumed a general absorption[1] such as is indicated by the dotted line of figure 20. The deviations from this dotted curve have been ascribed to the effect of the narrow bands. The intensity of each band is determined by taking the ratio of the diminution of the transmission which it produces to the transmission which would be expected if the general absorption only were present.

Both the absorption bands and the fluorescence bands have been indicated in figure 20 by lines whose lengths are proportional to the intensities of the bands. If a line is drawn through the ends of the lines that give the intensity of the absorption bands a curve (A) is obtained which is very similar in form to the absorption curve for a substance having a single broad band. This curve also has the same position with reference to the envelope of the luminescence bands (F) that the absorption curve in such cases has to the luminescence curve. It appears highly probable that just as a broad luminescence band may result from the overlapping of a group of bands, so the absorption of the same substance may result from the overlapping of a similar group of absorption bands.

The transmission curve for a thin layer of powdered uranyl sulphate is shown in figure 21, the source of light being an acetylene flame. In its general features this curve is similar to that for the double sulphate of uranyl and potassium. The fluorescence of the sulphate is not so brilliant and the fluorescence bands therefore show less prominently. The sulphate, as has been shown in a preceding paragraph, has the peculiarity of possessing two series of fluorescence bands lying close together, one set of bands being much more intense than the other. It will be noticed that the absorbed bands are also double. If we think of the more intense luminescence bands as constituting the principal series and the less intense bands forming a secondary series, a curious reversal is noticeable as we pass from the region of fluorescence to the region of absorption. Each band of the principal series in the luminescence region lies a little to the right of the corresponding band of the secondary series. The positions of the bands are indicated by short vertical lines in the lower part of figure 21, the bands of the secondary series being represented by dotted lines. When we pass to the absorption series, however, the more intense band lies to the left in each case. For example, the absorption band at 4,925 corresponds in position with a fluorescence band of the principal series; but the absorption band at 4,880, which probably corresponds to the band 4,890 of the secondary fluorescence series, is by far the more intense of the two.

[1] The fact that all the uranyl salts, so far as known, increase rapidly in opacity as the wavelength of the transmitted light decreases, even when the bands are greatly reduced in width by cooling, seems conclusive as to this assumption.

It will be observed that the absorption bands of uranyl potassium sulphate occurring at 4,760 and 4,920 (fig. 20) appear to coincide in position with two of the luminescence bands of the same substance. In other words, these two bands are "reversible" and may appear either as absorption bands or as luminescence bands, according to the conditions under which they are observed. The double sulphate thus shows the same phenomenon that was first described by H. Becquerel[1] in 1885 in the case of uranyl nitrate.

FIG. 21.—Transmission of a thin layer of uranyl sulphate.

It was, however, of interest to study these relations in the case of the uranyl spectra at ordinary temperatures also. Special precautions were necessary, for when a luminescence band occurs in a region where there is appreciable absorption it is clear that the apparent position of the crest of the band may be influenced by absorption in case the latter is not uniform. Where measurements of absorption are made with light containing rays that are capable of exciting fluorescence there may also be a displacement of the crest of the absorption band, owing to the presence of luminescence. There could be no displacement of

[1] Comptes Rendus, vol. 101, p. 1252. 1885.

this sort in case the light emitted were strictly proportional to the coefficient of absorption; but if the fluorescence band and the absorption band do not exactly coincide in position or in form, such a displacement is to be expected.

In order to avoid the necessity of changing the adjustment of the spectrophotometer, or the position of the substance, between measurements a thin layer of the uranyl potassium sulphate was in some cases mounted permanently in front of the slit. To locate the absorption bands the slit was illuminated, through the specimen, with light from an acetylene flame. To observe the luminescence bands a piece of blue glass was placed in front of the flame, so as to cut off the rays having the same wave-length as the bands, while permitting the exciting rays to pass; or in some cases the acetylene flame was replaced by a mercury arc. To guard against the presence of fluorescence in measurements of absorption a green glass was sometimes used.

With the relatively thick specimen first used the absorption was so great that the band at 4,760 could not be observed. The band at 4,920 was well defined, however, and could be accurately located. If the eyepiece pointer was set at the crest of the absorption band and the source of light then changed so as to bring out the fluorescence band, the latter was seen to be very obviously displaced toward the red. Photographs of the absorption and fluorescence spectra taken on the same plate also showed the relative displacement of the two bands very clearly. The wave-length of the fluorescence band as measured under these conditions was not the same, however, as that previously determined, and the whole appearance of the band was different from what had been observed when looking at the front surface of the luminescent substance.

More definite conditions for observing the absorption band were obtained by using nearly monochromatic light for transmission measurements. The spectrum of a Nernst glower was formed by a large spectrometer and a small region of the spectrum was isolated by means of a suitable screen containing a slit. The light coming through this slit, after passing through the specimen to be studied, fell upon the slit of the spectrophotometer. By suitable adjustment the center of the band of transmitted light could be made practically coincident with the center of the absorption band and the latter could be located with considerable accuracy. Under these circumstances the transmitted light contained no rays capable of exciting any observable fluorescence, so that we may look upon the determinations of absorption by this method as uninfluenced by errors due to the presence of luminescence.

Using a relatively thick layer, the absorption band was located at 4,919, while the crest of the fluorescence band (observed by transmission) lay at 4,974. An excessively thin layer, formed by depositing the salt from a solution, or suspension, in alcohol, gave a fluorescence

band whose crest was at 4,925, while the wave-length of the very faint absorption band was 4,922. Our previous determination of the wave-length of the luminescence band, when looking at the surface exposed to the exciting rays, was 4,920. These results appear to us to warrant the conclusion that if disturbances due to absorption could be entirely eliminated the two bands would be found to have exactly the same wave-length.

It must not be forgotten, however, that it is nearly impossible to observe the fluorescence spectrum under conditions which entirely eliminate effects due to absorption. The exciting light always penetrates to some extent beneath the surface, so that some of the emitted light must pass through the fluorescent material before it can reach the eye. It is natural, therefore, to expect a slight displacement in all cases. Although our most reliable measurement of the wave-length of the absorption band, 4,919, and our best determination of the crest of the luminescence band, 4,920, differ by less than the probable errors of measurement, we feel that it is not unlikely that the difference is a real one, due to the cause just cited.

The absorption band at 4,760 in the double sulphate differs in position by 5 units from the fluorescence band at 4,765. A portion of this difference may also be explained by absorption. But it is probably chiefly due to the difficulty in accurately locating the crests of these bands. The fluorescence band is extremely faint, while the absorption band is not very sharp, because of the large general absorption in this region.

Using a thick layer, formed by grinding down a translucent mass of adhering crystals until a piece about 0.5 mm. thick was obtained, a faint absorption band was observed at 5,127. This corresponds to the brilliant fluorescence band at 5,130. In all likelihood the coincidence here is complete, since measurements of the fluorescence band made at the same time and with the same specimen as that used for absorption measurements gave the same wave-length, 5,127, for both bands.

EXCITATION BY LIGHT CORRESPONDING TO DIFFERENT PARTS OF THE ABSORPTION REGION.

It seemed a matter of some interest to determine the relative effectiveness of light of different wave-lengths in producing fluorescence, and experiments having this end in view have been made in the case of the double sulphate. We were particularly interested in determining whether wave-lengths falling within the sharp absorption bands at 4,918, 4,760, 4,615, etc., were especially effective in exciting luminescence.

The source of the exciting light used in these experiments was a Nernst glower which was mounted in place of the slit of a spectrometer. The spectrum was focussed upon an opaque screen containing a narrow slit, and the light passing through this slit was used in exciting the speci-

men tested. The fluorescence spectrum was observed in a spectrophotometer, the specimen being set up at an angle of approximately 45° with the path of the exciting light, so that the collimator of the spectrophotometer could be pointed at the illuminated surface without interfering with the exciting light. Enough of the exciting rays were reflected into the spectrophotometer to enable the range of wave-lengths used in each case to be determined. The spectrophotometer was then set at the crest of the principal fluorescence band and the intensity measured by comparison with an acetylene standard. Observations of this sort were repeated throughout the absorbing region. The results are shown in figure 22. It will be noticed that the regions of strong excitation at 4,910 and 4,775 correspond very closely to the two absorption bands at 4,920 and 4,766. Some slight indication is also present of the other absorption bands. It is clear, however, that the ability to excite luminescence is not confined to rays falling within the narrow absorption bands, but extends to the region of general absorption lying between. It is not possible to determine the specific exciting power of different rays, as has been done in the case of eosin and resorufin,[1] because of our ignorance of the absorbing power of the salt for different wave-lengths.[2] The results indicate, however, that the specific exciting power varies only slightly with the wave-length, as in the case of resorufin and eosin.

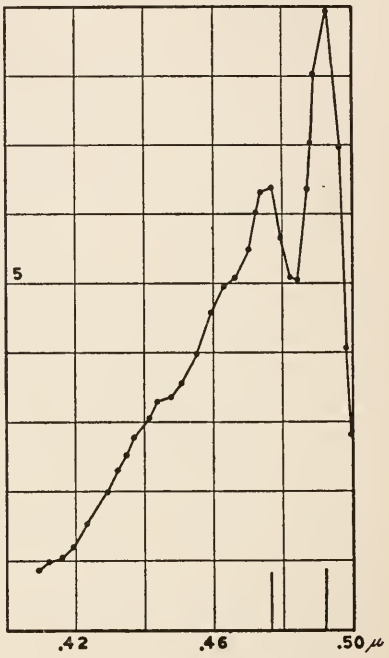

FIG. 22.—Intensity of fluorescence (ordinates) produced by exciting light of different wave-length (abscissæ).

THE RELATION BETWEEN ABSORPTION AND FLUORESCENCE AS IT APPEARS AT ORDINARY TEMPERATURES.

In 1885 H. Becquerel[3] made measurements of the spectrum of uranyl nitrate from which it would appear that the frequency interval remains constant in passing from the fluorescence to the absorption spectrum and that the suggestion of E. Becquerel in his classical memoir of 1872, that the emission bands and absorption bands belong to the same series, is in accordance with the facts.

H. Becquerel also showed that two of the bands are reversible, appearing as emission bands when suitably excited, whereas if light free

[1] Physical Review, XXXI, p. 381.
[2] The distribution of energy in the spectrum of the Nernst glower also has not been determined.
[3] H. Becquerel, Comptes Rendus, 101, p. 1252.

from exciting rays be passed through the substance, absorption bands in the same location are observed.

In our own work upon uranyl nitrate and potassium uranyl sulphate we have confirmed the results of H. Becquerel so far as the existence of reversible bands is concerned and have found for these substances 3 such bands instead of 2.

The frequency interval between absorption bands, like the fluorescence interval, is approximately constant, but, as may be seen from tables 12 and 13, it is much smaller.

Additional evidence on this point will be found in the chapters dealing with the double chlorides and with the spectra at low temperatures, where it will be established as a relation common to all uranyl spectra. The study of the absorption spectra at +20° C. is uncertain and unsatisfactory, because we have to do with unresolved groups of bands, and these two examples will suffice to illustrate the remarkable way in which the two frequencies interlock where fluorescence goes over into absorption.

TABLE 12.—*Absorption and fluorescence bands of potassium uranyl sulphate at +20° C.*

Absorption.			Fluorescence.		
μ.	$1/\mu \times 10^3$.	Interval.	μ.	$1/\mu \times 10^2$.	Interval.
0.4350	2298.9				
		62.8			
.4472	2236.1				
		68.8			
.4614	2167.3				
		66.5			
.4760	2100.8		0.4765	2098.6	
		68.3			**66.1**
.4920	2032.5		.4920	2032.5	
		82.0			83.2
.5127	1950.5		.5130	1949.3	
					83.6
			.5360	1865.7	
					81.9
			.5606	1783.8	
					83.4
			.5881	1700.4	
					84.9
			.6190	1615.5	

It will be seen from tables 12 and 13 that the last 3 fluorescence bands, counting from the red, are nearly or quite coincident with the first three absorption bands. Whether or not these coincidences are to be regarded as exact can not be determined from observations on unresolved spectra. It will be demonstrated later that reversals are exact between the ultimate components of bands, but not, in general, between unresolved aggregates.

That the fluorescence interval changes to conform to the absorption interval at the last step appears not only from the data in tables 12

and 13, but also in the determinations for other salts (tables 4 to 10) wherever the final fluorescence band (8) has been observed. The corresponding change in the absorption interval to conform with the fluorescence interval is much more difficult to establish, because the last absorption band toward the red is entirely invisible under ordinary conditions.

TABLE 13.—*Absorption and fluorescence bands of uranyl nitrate at +20° C.*

Absorption bands.[1]			Fluorescence bands.		
μ.	$1/\mu \times 10^3$.	Interval.	μ.	$1/\mu \times 10^3$.	Interval.
0.3830	2610.9				
		69.6			
.3935	2541.3				
		72.2			
.4050	2469.1				
		71.0			
.4170	2398.1				
		58.9			
.4275	2339.2				
		69.1			
.4405	2270.1				
		72.3			
.4550	2197.8				
		71.9			
.4705	2125.4		**0.4708**	2124.0	
		72.0			**70.2**
.4870	2053.4		**.4869**	2053.8	
		87.2			86.6
.5086	1966.2		**.5086**	1966.2	
					89.7
			.5329	1876.5	
					86.0
			.5585	1790.5	
					85.8
			.5866	1704.7	
					88.7
			.6188	1616.0	

[1] Absorption bands, excepting that at 0.5086 are from measurements by Jones and Strong (Am. Chem. Journal, 1910).

EFFECT OF WATER OF CRYSTALLIZATION—BEHAVIOR OF SOLUTIONS.

The effects of water of crystallization and the comparison of the spectra of the solid uranyl compounds with those of their solutions are to be treated at some length in subsequent chapters. A few points which have been brought out in the course of our work on the spectra at +20° C. are, however, recorded here.

The effect of water of crystallization in the case of uranyl nitrate is to shift the luminescence bands slightly in the direction of the longer waves. (Compare the hexahydrate with the anhydrous form in table 1.) This is the effect which it would seem most natural to expect, since the mass of the vibrating system is increased by the addition of water of crystallization without any increase, so far as we know, in the elastic

forces of the system. In fact, the presence of water so intimately associated with the salt molecule would probably increase the effective dielectric constant of the region in which the vibrations occur, and would thus cause a decrease in frequency quite independent of any effect due to increase in mass.

It has been shown by Deusen[1] and by Jones and Strong[2] that the absorption spectrum of the crystallized nitrate is nearly coincident with the absorption spectrum of the aqueous solution. In many cases no difference can be detected in the wave-length of the band in solution and in the solid crystal. In the case of other bands, however, the difference appears to be too great to be accidental. It seems not unlikely that the absorption spectrum contains several series of bands, some of which occupy almost identically the same positions for the solution as for the solid salt. We must assume, therefore, that at least a part of the dissolved salt has the same molecular structure as the solid crystals.

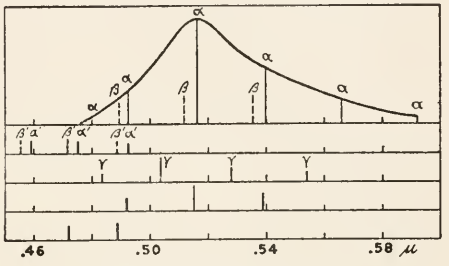

FIG. 23.—Position of fluorescence and absorption bands of uranyl sulphate.

In the case of the uranyl sulphate studied by us the phenomena are more complicated. As has already been shown, the luminescence spectrum of this salt, even at ordinary temperatures, contains two series of bands, which for convenience we shall designate the α and β series respectively. The α bands are by far the stronger and 6 of these could be observed. Of the relatively weak β bands only 3 could be seen. In the absorption spectrum of the solid salt 2 series of bands were also found (see fig. 21) which we shall call the α' and β' bands. Two of the α' bands corresponded in position with two of the α bands of luminescence, while one band of the β' series corresponded with one of the β bands. The wave-lengths are given in table 14 and are shown graphically in figure 23. It is a remarkable fact that while the α bands

TABLE 14.—*Uranyl sulphate fluorescence and absorption bands.*

Fluorescence:						
Crystals—Principal series (α)	4763	4929	**5148**	5395	5659	5925
Crystals—Secondary series (β)		4894	5098	5340		
Dehydrated salt (γ)		4843	**5049**	5285	5538	
Concentrated solution		4928	5145	5387		
Absorption:						
Crystals—α' series	4595	4755	4925			
Crystals—β' series	4555	4720	4880			
Concentrated solution		4718	4887	5095		

[1] Annalen der Physik, 43, p. 1128. 1898.

[2] American Chemical Journal, vol. XLIII, p. 37, 1910. See also Vogel, Spectralanalyse, p. 270, 1889.

are much the brighter in the luminescence spectrum, the α' bands in the absorption spectrum are much weaker than the β' bands.

The sulphate used in this experiment was in the form of small crystals, When the salt was dehydrated by being kept for about an hour in a stream of warm, dry air its luminescence spectrum was found to be absolutely different, each band being shifted toward the violet by about 100 Å. U. Brief exposure to the air apparently permitted a portion of the salt to return to the original condition, so that the original α and β bands could be seen as well as the γ bands characteristic of the dehydrated salt. In the case of a thin layer of the sulphate which had been dehydrated and then exposed for a short time to the air, each of the luminescence bands was found to consist of three overlapping bands, the components corresponding in position to the α, β, and γ bands respectively. Spectrophotometric measurements (with a rather wide slit) of the brightest luminescence band and of a portion of the absorption spectrum of the same layer are shown in figure 24. In the luminescence spectrum the β bands are by far the most prominent,[1] while in the absorption spectrum the α' bands are strongest and no γ' bands can be detected. The results point to the existence of two different hydrated salts corresponding to the α and β bands respectively, but further study would be necessary to make possible an entirely satisfactory explanation of the observed phenomena.

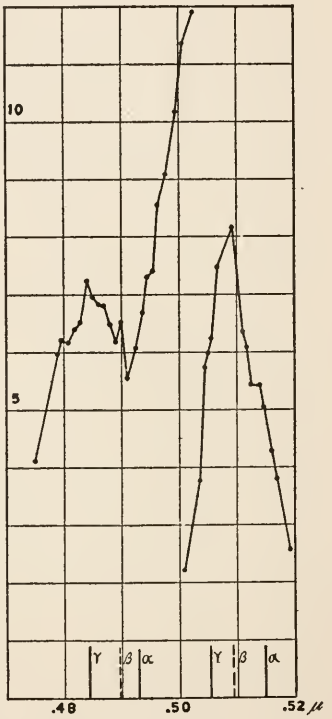

FIG. 24.—Uranyl sulphate (solid), showing the brightest fluorescence band at about 0.51 μ and a group of absorption bands at about 0.49 μ.

The concentrated aqueous solution of the sulphate showed weak fluorescence, and the three brightest bands, which could be located with reasonable accuracy, were found to agree in position with three of the α bands of the solid crystallized salt. In the absorption spectrum of the concentrated solution it was possible to locate three well-defined bands, two of which corresponded with two of the β bands of the solid salt (see fig. 25). The solution showed no trace of any fluorescence corresponding to the β series, nor did it show any trace of absorption corresponding to the α' series.

[1] The α' band appears in fig. 24 to be shifted by about 15 Ångström units toward the violet; whether this is a real shift, or whether it is due to disturbances caused by simultaneous absorption and luminescence we are unable to say.

In a concentrated solution of potassium uranyl sulphate (see fig. 26) three absorption bands were found at 4,910, 4,730, and 4,570. These

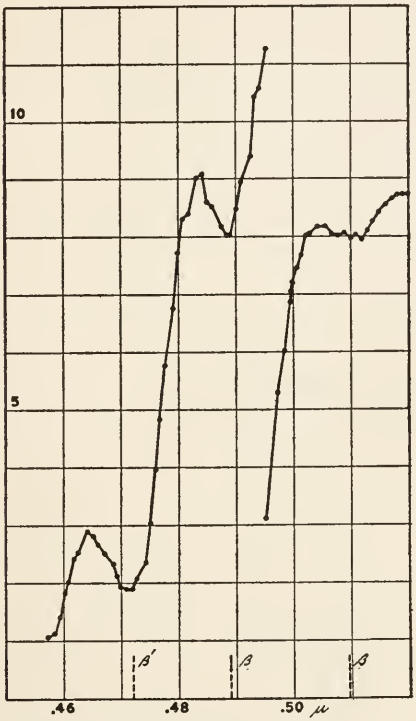

FIG. 25.—Uranyl sulphate (solution), showing at the left a portion of the transmission spectrum for a thin layer and at the right for a thick layer.

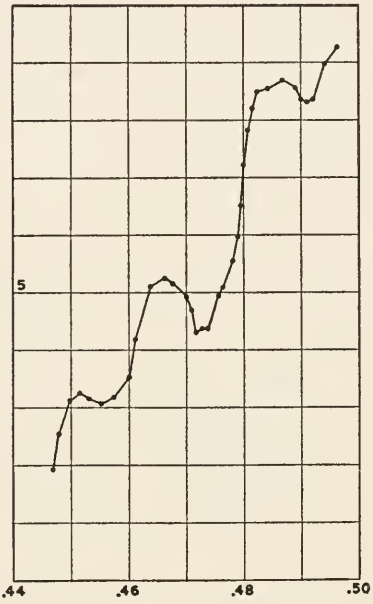

FIG. 26.—Transmission of a concentrated solution of uranyl potassium sulphate.

do not agree in position with the corresponding bands of the solid salt, which occur at 4,920, 4,760, and 4,472. The solution of the double sulphate shows no trace of fluorescence.

IV. PHOSPHORESCENCE OF THE URANYL SALTS.

Concerning the phosphorescence of the uranyl compounds, we find little on record beyond the early observations of E. Becquerel,[1] who, in his classic paper of 1861, noted the brilliant and very short-lived after-glow and made some observations on the law of decay.

For the study of the phenomena of phosphorescence in these substances and in other cases having a duration of glow of a few thousandths of a second, we devised a new instrument, the synchronophosphoroscope. Indeed, for the experiments to be described in this chapter, and which involved the use of surfaces of considerable size, the cooling of the substance during excitation, simultaneous observations during fluorescence and phosphorescence, etc., none of the existing forms are easily adapted. The original phosphoroscope of Becquerel,[2] later modified by E. Wiedemann,[3] and also the revolving drum type used successively in various forms by Becquerel,[4] Tyndall,[5] Kester,[6] and Waggoner,[7] afford sufficient speed, as does Merritt's[8] phosphoroscope of 1908; but none of these could be used without modification.

The new apparatus[9] consists of a small synchronous, alternating-current motor *A. C.*, figure 27, and a small direct-current motor *D. C.* upon a common shaft. To one end of the shaft is attached a sectored disk, *WW*, figures 27 and 28, with four equal open and four closed sectors, corresponding to the four poles of the *A. C.* motor. On the circuit of 60 cycles this machine, when brought to speed by the *D. C.* motor and released, runs steadily at 30 revolutions per second. A "step-up" transformer *TT*, in the same alternating-current circuit, produces discharges at the spark-gap, or series of gaps (*E*), at each alternation, *i. e.*, 120 times a second. This discharge may be reduced to a single spark by proper adjustment of the resistance and capacity of the circuit, or more conveniently for many purposes the discharge may be confined to the peak of the wave by means of the four-pointed star-wheel *SS* (figs. 27 and 28), which is mounted on the shaft and carefully adjusted as to phase.

The direct-current motor may also be used to drive the sectored disk at other speeds, in which case the circuit of the motor *A. C.* is broken and the discharge is derived from any convenient source capable of producing a proper spark at each quarter revolution.

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[1] E. Becquerel. Annales de Chimie et de Physique (3), LXII, p. 1. 1861.
[2] *Ibid.*, LV, p. 5. 1859.
[3] E. Wiedemann, Wiedmann a Annalen, XXXIX, p. 446, 1888.
[4] E. Becquerel, l. c.
[5] Tyndall. See Lewis Wright's volume on light, p. 152. London, 1882.
[6] Kester, Physical Review (1), IX, p. 164.
[7] Waggoner, Carnegie Inst. Wash. Pub. No. 152.
[8] Nichols and Merritt, Carnegie Inst. Wash. Pub. No. 152.
[9] E. L. Nichols: Proc. Nat. Acad. of Sciences, v. 2, p. 328. 1916. Also Science, XLIII, p. 937. 1916.

When the sectored disk *WW* is so adjusted on the shaft that the closed sectors conceal the phosphorescent surface during excitation by the spark, an observer, looking through the open sectors as they pass, sees the phosphorescence as it appears a few ten thousandths of a second after. The apparatus is thus suitable for the study of phosphorescence of very short duration or of the earliest stages in cases of slow decay. By shifting the sector on the shaft it is possible without variation in

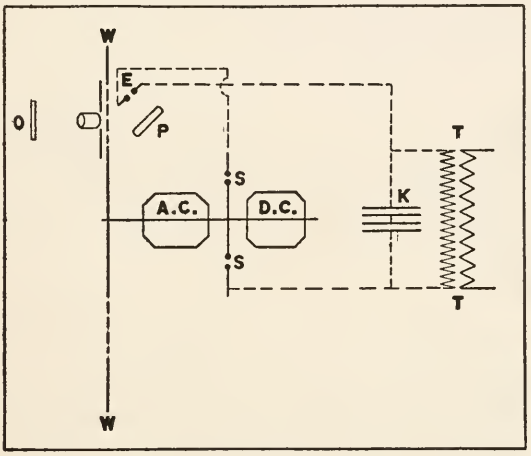


FIG. 27.

FIG. 28.

the rate of rotation to make observations at the very beginnings of phosphorescence and to compare, by simultaneous vision, the appearances just before and immediately after the close of excitation, or, on the other hand, the earlier with the later stages, up to about 0.004 second. The photometer, spectroscope, spectrophotometer, camera, etc., may all readily be used with this form of phosphoroscope and studies of the most varied character become possible.

Phosphorescence is commonly regarded simply as the after-effect of fluorescence, the emission spectrum immediately after the close of excitation being identical with that immediately before excitation ceases. This has hitherto been only an assumption, since it is thinkable that the process which prepares a substance for phosphorescence might produce emission during excitation differing from that which constitutes phosphorescence and which together with the latter would be present during fluorescence. It is also thinkable, although unlikely, that the phosphorescence might contain some components requiring a measurable time for development and observable only after an appreciable interval.

This is a matter which it would be very difficult to settle in the cases of phosphorescence hitherto studied, because the spectrum of fluorescence and phosphorescence consists of broad bands or complexes of overlapping bands, and almost the only criterion of identity is that of color.

The uranyl salts, because of their remarkable spectra, afford an unusual opportunity to establish the exact relation between the emission of light during excitation and at various times after excitation has ceased, and it was for this purpose that the first experiments with the new phosphoroscope were undertaken.

The method, briefly outlined, is as follows: The substance, inclosed in a flat tube of glass *BA* about 8 cm. long and 2 cm. wide, is viewed through the rapidly revolving sectored disk of the synchrono-phosphoroscope. It is mounted vertically, with its axis at right angles to the radius of the disk, as shown in figure 29.

FIG. 29.

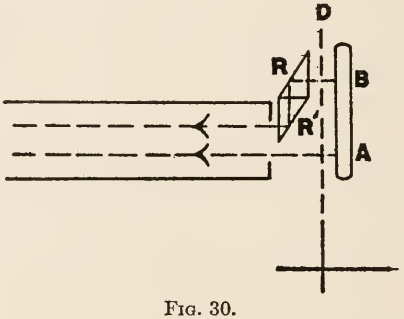


FIG. 30.

It is uniformly excited by zinc sparks 120 times a second while hidden by the closed sectors and is visible for 1/240 of a second during the passage of each of the intervening open sectors.

A phosphorescent substance of slow decay appears under these circumstances to be equally bright from top to bottom, but if one of the uranyl salts, such as the double uranyl-ammonio sulphate, which was the substance selected for detailed study, be used, it appears a very bright green at the bottom of the tube, shading off to bare visibility at the top.

The rate of decay of this substance and of the other uranyl salts is so rapid that the upper end of the tube, which is seen at the intensity which corresponds approximately to the instant 0.003 second after excitation, has only a small fraction of the brightness of the lower end, which is viewed about 0.0005 second after excitation.

The particular salt mentioned above was selected because at low temperatures its spectrum is unusually well resolved in groups of complexes of narrow, line-like bands, making it possible to detect changes in the individual components.

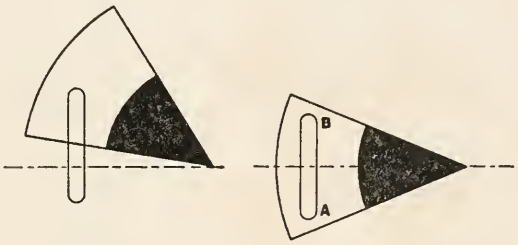
To obtain simultaneous observations a pair of right-angled prisms was mounted before the slit of a Hilger spectroscope, as shown in figure 30.

Light from the lower end of the tube *A* enters the lower half of the slit. That from the upper end *B*, after two total reflections, enters the upper half of the slit, and we have two spectra one above the other,

coinciding throughout as to wave-length, but separated by a dark line formed by the lower edge of the second prism (R').

To compare fluorescence with phosphorescence, the sectored disk was shifted upon its shaft until the lower end of the tube was viewed during excitation, the upper end immediately after (fig. 31*a*). To compare the phosphorescence spectrum at an earlier and later stage, the disk was so set that its position at the moment of excitation was as shown in figure 31*b*. By means of the reflecting prisms at the slit of the spectroscope, already described, the spectrum of the light emitted from region A was compared with that at B in each case. At +20° C. the banded spectra were found to be identical in every respect, except in brightness; and the same was true at low temperatures, where it was possible to inspect each of the numerous line-like bands individually.

Fig. 31*a*. Fig. 31*b*.



Of the seven homologous series distinguishable in the fluorescence spectrum, all were present in phosphorescent light, unshifted as to position and not perceptibly enhanced or diminished in relative brightness.

The comparison was less satisfactory as regards minor details in the case of the early and late stages of phosphorescence, some of the fainter bands being invisible, but changes such as might be looked for, *i. e.*, those due to the greater persistence of certain series, could scarcely have escaped notice.

The significance of these observations is two-fold: On the one hand we find that for the only examples of luminescence which admit of such detailed inspection *the spectrum of phosphorescence is identical with that of fluorescence*, and since there are no indications to the contrary in the case of other classes of substances thus far studied, it is probable that the above statement will apply to all phosphorescent materials. On the other hand, we find that, in spite of its great complexity, the luminescence spectrum of a uranyl salt is to be regarded as a unit, all its components decaying at the same rate after the cessation of excitation.

Thus this class of substances (*i. e.*, the uranyl salts) not only conform to the first three criteria of homogeneity discussed in Chapter II but likewise to that based upon the phenomena of phosphorescence.

CURVES OF DECAY.

To determine the change of intensity of phosphorescence with the time a simple form of photometer previously used in a study of the phosphorescence of kunzite[1] was mounted in front of the sectored disk.

[1] Nichols and Howes, Physical Review (2), IV, p. 19. 1914.

A lateral strip of the phosphorescent salt 1 cm. wide was excited by sparks from a single spark-gap between zinc terminals and measurements of the brightness were made at various times after the close of excitation. The necessary conditions were attained by shifting the disk successively through small angles, so as to vary the interval between excitation and observation. The time could be estimated with sufficient accuracy by noting the instantaneous positions of the disk for each adjustment, as given by the strictly synchronous illumination due to the spark.

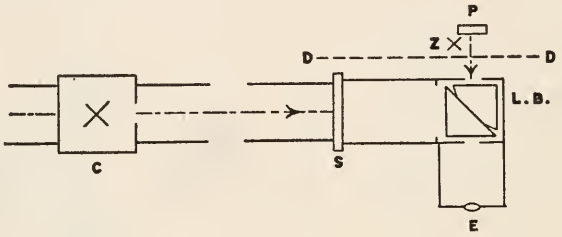


FIG. 32.

The arrangement of the apparatus is shown in figure 32, in which P is the phosphorescent surface, DD the sectored disk, $L.\ B.$ the Lummer-Brodhun cube of the photometer, E the eyepiece, S a color-screen and matte translucent plate, C the comparison lamp which traveled along the track of an optical bench. The cross at Z indicates the position of the spark-gap.

In table 15 relative intensities I, the reciprocals $1/\sqrt{I}$, and times T after excitation are given. Figure 33 shows the relations between I and T, and $1/\sqrt{I}$ and T respectively in the usual manner.

TABLE 15.

$T.$	$I.$	$1/\sqrt{I.}$	$T.$	$I.$	$1/\sqrt{I.}$
0.000479	59.49	0.130	0.00170	2.03	0.702
.000637	27.78	.190	.00193	.971	1.014
.000856	16.02	.250	.00212	.610	1.280
.000949	12.62	.281	.00247	.296	1.836
.00110	9.80	.319	.00287	.159	2.524
.00146	5.03	.446			

As appears from the table and curve ABC, figure 33, this substance exhibits a remarkably rapid decay, falling in the interval between 0.0005 second after close of excitation and 0.003 second to less than three-thousandths of its intensity at the beginning of that interval. To show the degree of accuracy with which the lower intensities were observed, the portion of the curve BC is reproduced with ordinates magnified ten times $B'C'$. The results are likewise plotted in the customary manner with $1/\sqrt{I}$ as ordinates (curve DEF), and this brings

out an unusual characteristic. It is usual to find two processes of phosphorescence succeeding one another and represented by the two straight arms of the curve *DE* and *FG*, but in all the numerous cases hitherto described, excepting two to be discussed in a subsequent paragraph, the later process (*FG*) is indicated by a curve of lesser slope. In the case of this uranyl salt, however, *FG* trends very sharply upward, showing a greatly accelerated decay.

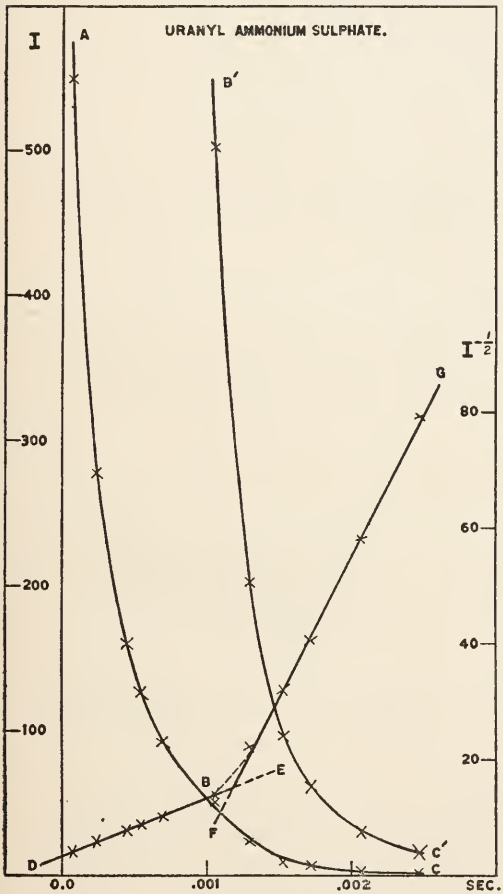


FIG. 33.

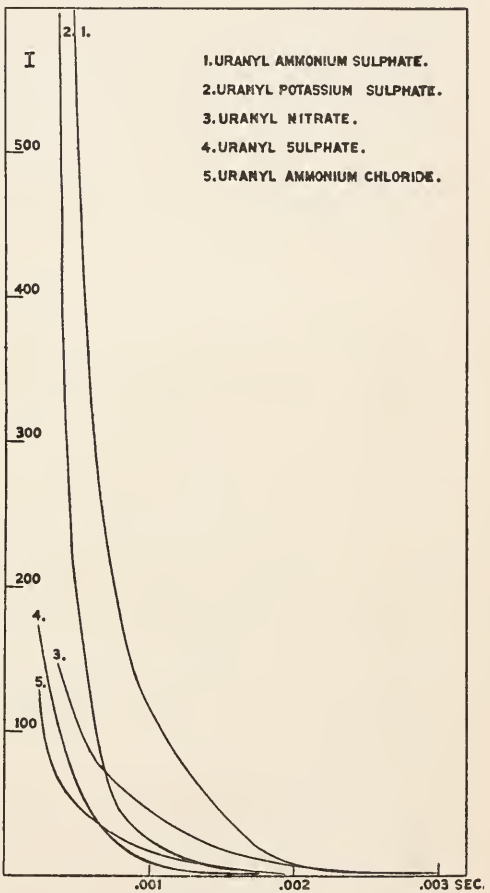


FIG. 34.

By means of these preliminary observations certain facts may be regarded as established.[1] These may be summarized as follows:

(1) There is no appreciable change of color during decay.

(2) The decay of phosphorescence is exceedingly rapid, the intensity falling to one-thousandth of its initial value within 0.0035 second.

(3) The very complex fluorescence spectrum at $-180°$ C. is identical in structure and relative distribution of intensities with that observed during the earlier and later stages of phosphorescence.

[1] Nichols, Proceedings National Academy of Sciences, vol. II, p. 328. 1916.

(4) The curve of decay of phosphorescence differs from the prevailing type in that although as usual two successive processes are distinguishable, the second process is more rapid instead of being slower than the first.

The study of these phenomena has since been extended to several other typical uranyl salts, the curves of decay of which were determined by the method just described and under conditions of excitation, etc., as nearly constant as possible.[1] These curves of decay are of the same new type originally found in the uranyl ammonium sulphate. The two processes, as determined by the customary method of plotting $I^{-1/2}$ as a function of the time are indicated by straight lines differing from one another in slope and the second process has in all cases the steeper gradient. Later experiments, in which the intensity of excitation was increased, revealed the presence of a third process not included within the interval of time covered by our earlier experiments.

STUDIES INVOLVING THE FIRST AND SECOND PROCESSES.

The curves shown in figures 34 and 35 are typical of the results obtained with all the salts under observation. They represent the decay of the phosphorescence of the compounds shown in table 16.

The initial intensity, under like excitation, varies greatly in the different salts, as also, to some extent, does the rate of decay. It will be noted that the initial intensities of the ammonium and potassium sulphates, for example, are several times greater than those of the nitrate, the sulphate, and the ammonium chloride. This is, however, a question of previous history as well as of chemical and physical constitution, as was determined in the following manner:

TABLE 16.

Curve.	Substance.
1	Uranyl ammonium sulphate.
2	Uranyl potassium sulphate.
3	Uranyl nitrate + $6H_2O$.
4	Uranyl sulphate.
5	Uranyl ammonium chloride.

Uranyl potassium sulphate was dissolved in hot water and a mass of the minute crystals which were thrown down on cooling the solution were immediately sealed up in a glass tube. Care was taken throughout these manipulations to protect the precipitate from the action of light.

This sample, still in darkness, was mounted in the synchrono-phosphoroscope and a curve of decay was taken, the first exposure to exciting light being that at the beginning of the run. The substance then showed, temporarily, a brilliancy of phosphorescence much above that to be obtained under ordinary circumstances, but was soon reduced to its normal and semi-permanent condition, after which the usual curve of decay was obtained.

[1] Nichols and Howes, Physical Review (2), IX, p. 292. 1917.

EXCITATION IN THE PRESENCE OF RED AND INFRA-RED RAYS.

To determine whether red or infra-red rays have an effect on these substances similar to that observed in the case of the phosphorescent sulphides, a modification of the apparatus was made such that the surface under examination could be subjected to the intense illumination obtained by focusing the crater of an electric arc upon it. A screen of excellent ruby glass was interposed to cut off all but the longer waves and observations were made through a screen quite impervious to red.

Exposure to this source was found to affect measurably neither the brightness of fluorescence nor of phosphorescence. Curves taken after exposure to this source, those taken with the substance subjected to it interruptedly throughout the run, and curves in the determination of which readings were taken alternately with and without red light were all identical with those taken in entire absence from such exposures. The striking contrast between this negative result and the well-known effects of infra-red radiation upon the phosphorescence of the sulphides is notable.

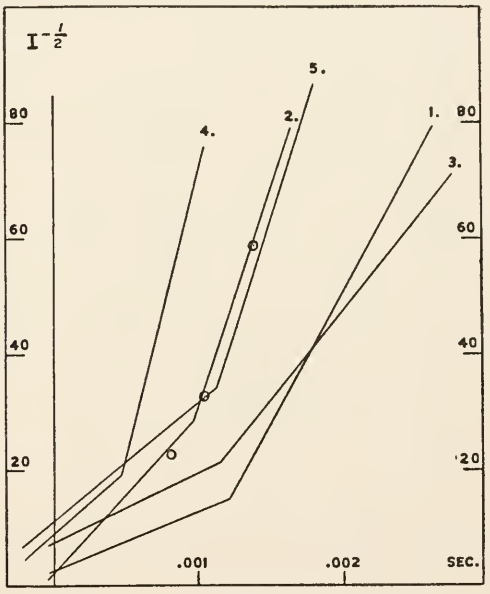


FIG. 35.

The observations already cited, showing the complete identity of the spectrum of fluorescence with that of phosphorescence seemed to indicate that the intensity would go over from that of fluorescence to that of phosphorescence without discontinuity. This conclusion was confirmed, within the errors of observation, by measurements just before and after the close of excitation. The only previous instances where this relation has been experimentally established, so far as we know, are to be found in Waggoner's[1] studies of phosphorescence of short duration and in recent observations on the luminescence of kunzite.[2]

In view of the unexpected character of the decay curves for the phosphorescence of the uranyl compounds, the question arises whether the rather unusual mode of excitation employed, *i. e.*, periodically repeated exposures, 120 times a second, to groups of sparks of high frequency, might produce such a result, or whether the decay curves are character-

[1] Waggoner, Physical Review, XXVII, p. 209.
[2] Nichols and Howes, Physical Review (2), IV, p. 26.

istic of this class of compounds, whatever the mode of excitation. It is true that both Waggoner[1] and Zeller,[2] using a Merritt phosphoroscope, found in their studies of phosphorescence of short duration that excitation by means of a spark discharge very similar to our own gave decay curves of the usual type.

It is also obvious from the measurements already described that the interval between excitation, *i. e.*, 1/120 second, is sufficient for the complete discharge of the phosphorescent glow, and since the absence of any effect of red and infra-red indicates that there is no storage of undeveloped energy to be carried over, such as occurs in the phosphorescent sulphides, it seems probable that the decay curves do not vary greatly from that which might be obtained, were it possible to make the experiment, from a single exposure.

To test this a run was made upon the sample of uranyl ammonium sulphate previously used, but with the Merritt phosphoroscope.

By driving the disk of this instrument 3,000 revolutions a minute, much the same range of time intervals was available as with the synchrono-phosphoroscope.

To further vary the conditions, a quartz mercury arc was substituted for the spark-gap of Waggoner and Zeller. The arrangement of apparatus was as shown in figure 36, in which *DD* is the revolving disk, *H* the mercury lamp, *P* the phosphorescent substance, *LB* the Lummer-Brodhun cube of the photometer, *SS* a color-filter and milk-glass screen. The device for shifting the oblique mirror *M* with reference to the aperture *A* in the disk is not shown.

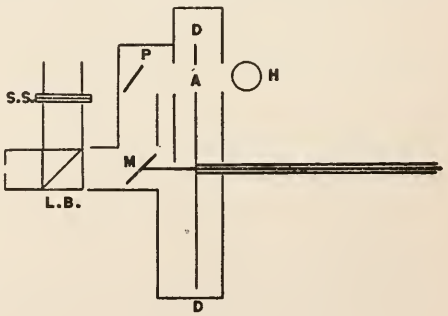


Fig. 36.

Although the decay was somewhat more rapid in this determination on account of the less intense excitation, the curve was of precisely the type obtained by the previous method.

Measurements upon some of the bands of brief duration in the spectrum of the phosphorescent sulphides, recently made with the synchrono-phosphoroscope under experimental conditions identical with those here described,[3] yield curves of the usual type associated with these sulphides, so that the question of the change of form being due to the phosphoroscope employed is effectually eliminated.

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[1] Waggoner, Physical Review, xxvii, p. 209.
[2] Zeller, Physical Review, xxxi, p. 367.
[3] Nichols, Proc. Am. Philosophical Society, lv, p. 494. 1916.

SOLID SOLUTIONS AND SEMI-FLUIDS.

The uranyl salts differ from nearly all if not all phosphorescent substances hitherto studied. We do not have, as in the phosphorescent sulphides, the preparations of Waggoner, the ruby, etc., to deal with a trace of active material in solid solution, but with compounds that are in themselves brilliantly phosphorescent. If the peculiar character of the curve of decay is due to that fact it might be expected that uranium

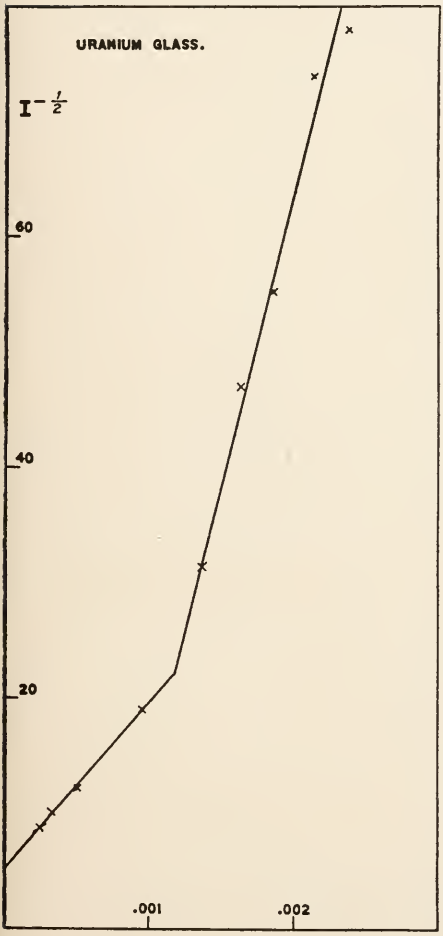

FIG. 37

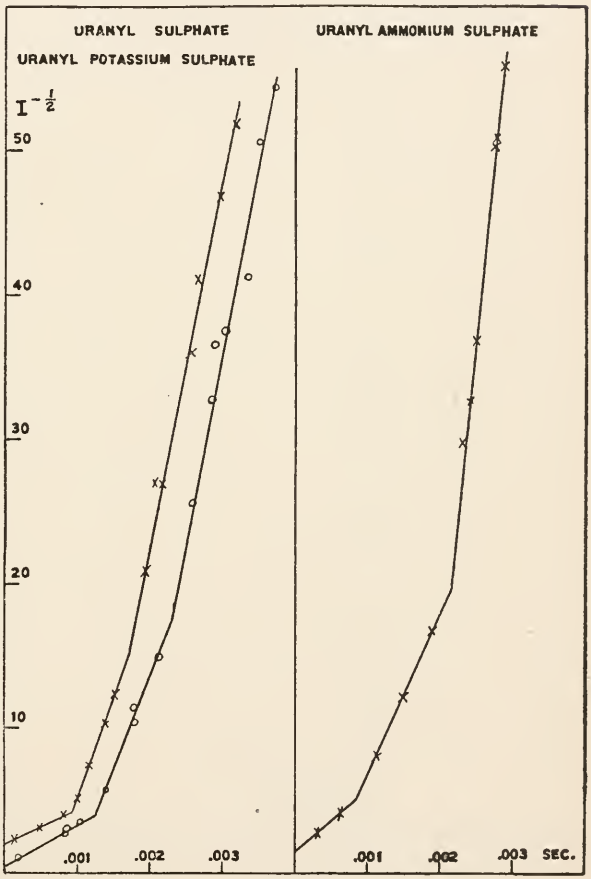

FIG. 38.

glass, in which the active material is considered to be in a state of solid solution, would have a law of decay corresponding to the prevailing type for such solutions, *i. e.*, with the first process as indicated by the curve for $I^{-1/2}$, and time, represented by a line of steeper slope than the line for the second process. A piece of uranium glass gave, however, a decay curve similar to those of the uranyl salts (see fig. 37). Another

preparation which differs from most of the uranyl salts is the uranyl sodium phosphate, a sample of which was made by D. T. Wilber for certain studies in fluorescence recently published.[1] This substance is a very viscous liquid with the characteristic green fluorescence of the uranyl compounds.

One might expect, in accordance with the findings of Becquerel for liquids in general,[2] that there would be no observable after-glow. It

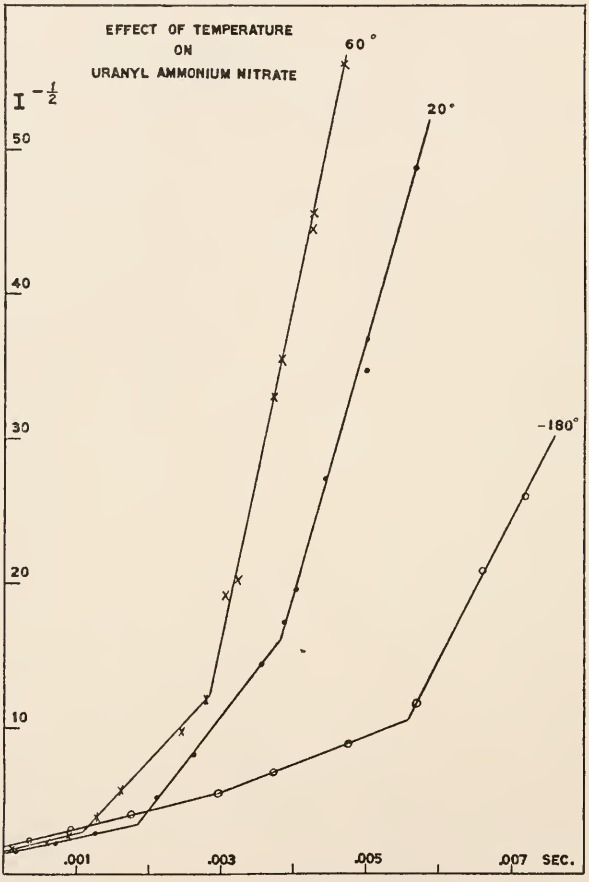

FIG. 39.

is true that Becquerel expressed the belief that with a phosphoroscope of sufficient speed, phosphorescence would probably be detected in fluorescent liquids, but no one, so far as we know, save Dewar in an unconfirmed statement concerning a supposed phosphorescence of liquid air, has since that time (1859) recorded an instance of phosphorescence excepting in solids and gases.

When a tube containing the phosphate was tested with the synchrono-phosphoroscope no phosphorescence was found of duration

[1] Howes and Wilber, Physical Review (2), vol. 7, p. 394. Mar. 1916.
[2] See E. Becquerel, La Lumiere, vol. 1, chapter on Phosphorescence.

sufficient to be detected. Another sample so prepared as to reduce the amount of water to a minimum did, however, exhibit phosphorescence of measurable duration. This preparation, so slow was its rate of flow, might be regarded as a plastic solid rather than a viscous liquid. A bead of microcosmic salt, colored in the usual manner with uranium oxide, was comparable in its phosphorescence with canary glass.

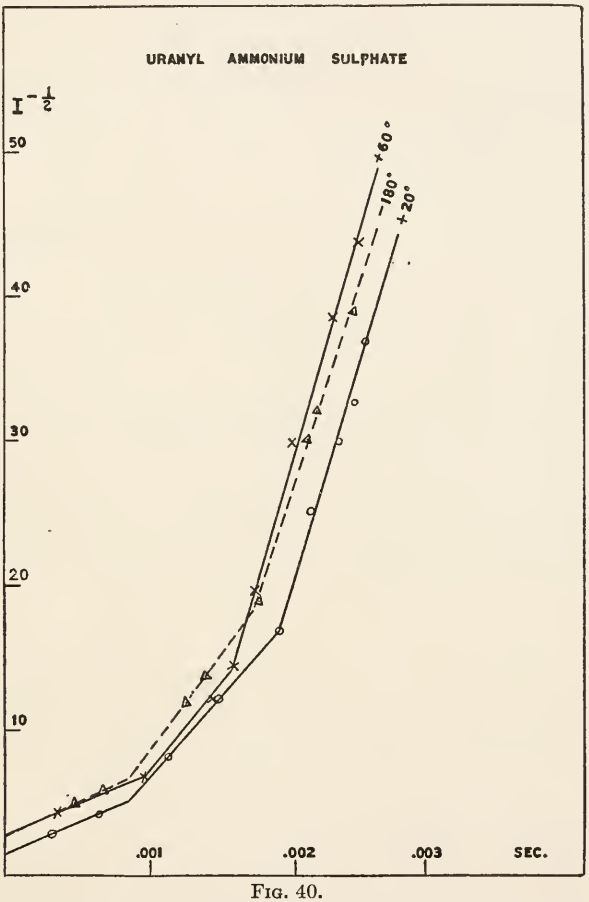

FIG. 40.

It appears that the persistence of luminescence is due to the consistency of the substance and disappears as the fluidity increases; also that the peculiar type of decay here described is common, not only to the crystalline uranyl salts in general, but also to the gelatinous forms, as in this double salt, and to substances in which uranium appears in solid solution, as in the case of the canary glass.

THE THIRD PROCESS.

E. Becquerel,[1] in the course of his great pioneer work on phosphorescence, made a number of observations on the uranyl salts and on

[1] E. Becquerel, Annales de Chimie et de Physique (3), LXII, p. 1. 1861.

uranium glass. He noted the brilliant initial intensity and very rapid decay, and to test the independence of the constant in his equation of decay when the illumination varied he made many measurements. If from his data we compute $I^{-1/2}$, as a function of the time, we obtain curves of the same general form as those in figure 32.

Becquerel's observations are not numerous enough, taken by themselves, to determine completely the type of curve. His measurements, however, cover a larger time interval than ours and the values for the longest times indicate an even more rapid decay following the second process. We had, indeed, found some indications of a similar tendency which had been omitted from our curves as lying almost beyond the range of definite determination.

To investigate the further trend of the curves of decay, the intensity of excitation was increased by readustment of the sparking circuit, by which means it was found possible to extend the time interval for more than 0.006 second beyond the cessation of excitation.

Careful, often repeated measurements, of the various salts showed in fact a third linear process beginning where our previous determinations had ceased and having a steeper slope, indicative of still more rapid decay. Typical results are indicated in figures 38, 39, 40, etc.

These processes may be numbered for convenience 1, 2, and 3 in the order in which they occur. Processes 1 and 2 are in general of about equal duration for a given salt. The abruptness of transition, however, varies greatly, and in some instances the change of slope is so gradual as to encroach seriously on process 2 at both ends.

THE INFLUENCE OF TEMPERATURE.

The only previous instances of decay of phosphorescence in which the later stages are more rapid than those preceding are noted by Ives and Luckiesh[1] in their study of the influence of temperature on phosphorescence, and by E. H. Kennard[2] in a more recent paper.

Ives and Luckiesh measured the phosphorescence of one of Lenard and Klatt's sulphides (BaBiK from Leppin and Masche). This substance was found to be very sensitive to change of temperature and the results at 0°, 22°, and 35°, C. when plotted for $I^{-1/2}$ and time in the usual manner, gave curves varying greatly in slope. The curve for 0° is concave toward the time axis, that for 22° linear, and that for 35° *strongly convex*. They show that a linear relation may be obtained for each of these curves by varying the exponent of I.

The effect of temperature in the case of the phosphorescent sulphides, where one has to do with a composite of many overlapping bands of varying duration, is undoubtedly different from that to be

[1] Ives and Luckiesh, Astrophysical Journal, XXXVI, p. 330 (1912).
[2] Kennard, Physical Review (2), IV, p. 278 (1914).

expected with the uranyl salts, where the spectrum, in spite of its complexity of structure, is a unit. It was deemed of interest, however, to determine the effect of temperature upon the latter.

For this purpose a specimen of the uranyl ammonium nitrate was mounted within a cylindrical Dewar flask with unsilvered walls and its decay of phosphorescence was determined with a synchrono-phosphoroscope at a temperature a few degrees above that of liquid air (about −180°) at +20° and at +60°. The last-named temperature was maintained during the run by means of an electrical heating-coil.

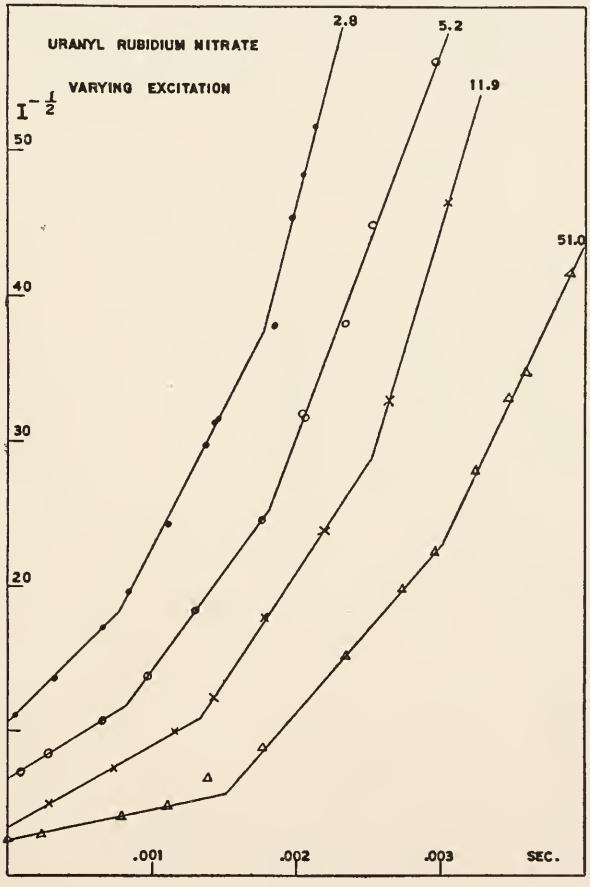

Fig. 41.

The principal change consists in a marked retardation of decay with lowering temperature (see fig. 39), but this is not a universal characteristic of the uranyl compounds. Uranyl ammonium sulphate, for example (fig. 40), is but slightly influenced in its rate of decay by change of temperature and the curve for −180° is intermediate between those for +20° and +60°.

THE EFFECT OF VARYING THE INTENSITY OF EXCITATION.

To determine the effect of the intensity of excitation, a series of measurements were made with the spark-gap at various distances from the phosphorescent surface. The substance observed in these experiments was uranyl rubidium nitrate. It was found possible to make observations of the decay of phosphorescence with the excitation reduced to a two-hundredth of that usually employed.

From the curves obtained, of which four are given in figure 41, it will be noted that all three processes are present, whatever be the intensity of the exciting light; also that, taken roughly, processes 1 and 2 are of nearly equal duration, and that with decreasing intensity of excitation the duration of each of these processes diminishes.

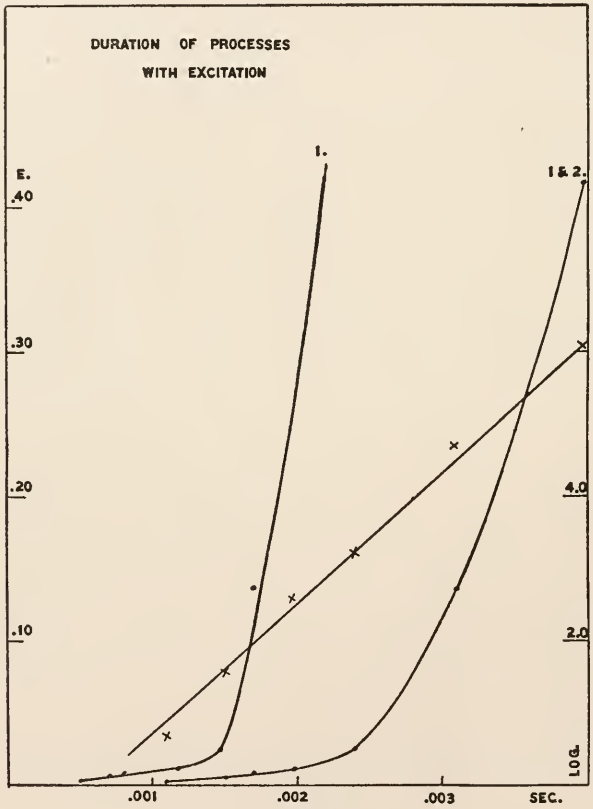

FIG. 42.

These relations are better shown in figure 42, in which the duration of process 1 and the sum of the duration of processes 1 and 2, counting from the close of excitation, are plotted, with the intensity of the exciting light as ordinates. Approximately in both cases the duration is proportional to the natural logarithm of the excitation. (See table 17.)

This decrease in the duration of the two processes with falling excitation affords an obvious explanation of the varying character of

the curves of decay of phosphorescent substances. Where the excitation is chiefly superficial, as in the case of some powders, the excitation may be nearly of one intensity and the curve made up of well-defined linear processes with sharp inflection-points. We have found this to be the case in many instances. Where, on the other hand, fluorescence is excited within the crystalline mass by rays that have suffered considerable loss by absorption, etc., there will be a wide range of intensities of excitation and a curve results with distributed knees and linear processes shortened and sometimes almost obliterated. We observed this particularly where a clear crystal was mounted with faces perpendicular to the photometer and was excited from behind so that the light emitted by the surface nearest the exciting source passed through

TABLE 17.—*Variation of length of processes with excitation (phosphorescence of uranyl rubidium nitrate).*

Intensity of excitation (E).	Nat. log. E.	Duration.		
		Process 1.	Process 2.	Process 1+2.
		sec.	*sec.*	*sec.*
41.70	6.033	0.0022	0.0018	0.00400
13.70	4.919	.00170	.0014	.00310
2.52	3.220	.00147	.000993	.00240
1.35	2.590	.00118	.00080	.00198
.900	2.190	.00080	.00090	.00170
.476	1.560	.00070	.00076	.00146
.201	.698	.00050	.00060	.00110

the crystal and was partially absorbed. Excitation occurred within the crystal in diminishing amount with increasing depth and the composite phosphorescence reaching the eye under such conditions showed this blending effect to a marked degree. The same crystal when excited from in front gave a curve in which the angles between processes were made more sharply defined. The effect in question is probably a general one and may well account for the perplexing differences in the curves of decay obtained under slightly varying circumstances. Thus, one observer will obtain an angular curve, where another, studying the same material, can detect no linear processes. The same observer, indeed, in attempting to repeat his measurements, will often find the above-mentioned change of type under conditions which seem to be identical but in which the same relations as regards superficial and internal excitation are not preserved.

We found in the study of this effect a crystal one smooth face of which gave the blended curve, while the opposite face, which was rough, gave the angular curve, a change produced and reproducible by merely rotating the crystal through 180°.

THE PHOSPHORESCENCE OF VARIOUS NITRATES.

Observations were made on a series of nitrates previously prepared for the detailed comparison of the fluorescence spectra of that salt.[1] These consist of crystals with 6 H_2O (rhombic), 3 H_2O (triclinic), and 2 H_2O (system undetermined) as water of crystallization and a specimen sealed in glass which had been rendered as nearly anhydrous as was possible without decomposing the nitrate.

The curves of decay indicate a much slower rate of decay for the crystalline forms than for the anhydrous nitrate. Whatever effect the amount of water of crystallization may have is doubtless masked by the far greater influence of the crystalline form. This is perhaps to be expected, since, as will be shown in Chapter VII, these specimens exhibit as great differences in the structure and appearance of their fluorescence and absorption spectra as commonly exist between entirely distinct uranyl salts. Similar differences in the case of salts similar in composition but differing in crystalline form will likewise be described in a subsequent chapter.

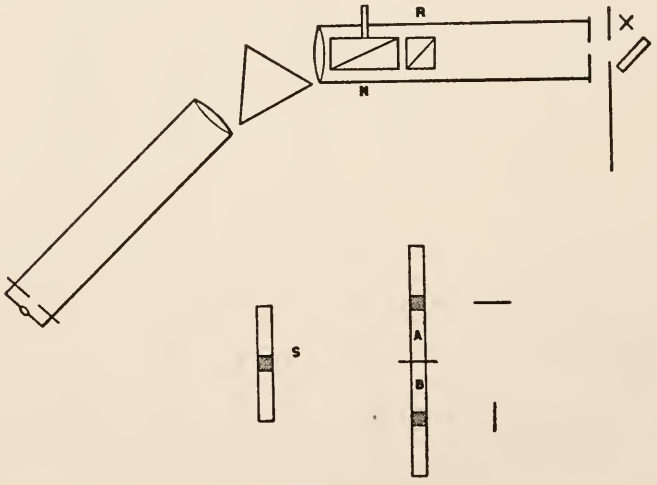

FIG. 43.

OBSERVATIONS ON POLARIZED PHOSPHORESCENCE.

Certain crystals of the double chlorides of uranyl exhibit fluorescence spectra consisting of sets of bands polarized at right angles to one another. To determine whether these components after the close of excitation decay independently or without change in their relative intensities, the following experiment was made:

A crystal of the rubidium uranyl chloride that exhibited the phenomenon of polarized fluorescence was mounted behind the disk of the synchrono-phosphoroscope and was observed with a spectroscope.

[1]Nichols and Howes; Physical Review (2), IX, p. 292. 1917.

The slit of the latter instrument was divided into two parts by means of an opaque strip across the middle (*S*, fig. 43).

Within the collimator a doubly refracting rhomb *R* and Nicol prism *N* were mounted. The rhomb gave two slit-images vertically displaced and the adjustment was such that the lower part (*A*) of one image was contiguous with the upper part (*B*) of the other.

Thus two spectra of the phosphorescent field were obtained corresponding to the two polarized components. These presented the usual distinctive structures at whatever stage of the phosphorescent decay they were observed. By rotation of the Nicol prism the two fields could be brought to equal brightness for any given part of the spectrum, and this balance, if made with the sector of the phosphoroscope set so as to give observations at 0.0005 second after extinction, was found equally correct up to 0.005 second or as long as phosphorescence was observable. The two components therefore decay at the same rate.

SUMMARY OF PHOSPHORESCENCE OF SHORT DURATION.

(1) All uranyl salts thus far examined possess the same type of phosphorescence; *i. e.*, with increasing instead of diminishing rates of decay.

(2) This is true not only of the crystalline forms, but also of uranyl compounds in solid solution or in the plastic state characteristic of the double phosphates.

(3) The initial brightness of phosphorescence under like excitation varies greatly with the different salts, as does also to some extent the rate of decay.

(4) The brightness of a salt newly prepared in darkness is greater when first excited than subsequently, but it soon reaches a nearly stable condition.

(5) Exposure to red and infra-red rays is without effect as regards the rate of decay.

(6) The phosphorescence, like the fluorescence, of the uranyl salts appears to be independent of the mode of excitation, and the structure of the intricate spectrum is the same during excitation and throughout the observable phosphorescent interval.

(7) Changes in the rate of decay are not continuous, but occur in definite steps, there being at least three successive processes within the interval covered by observations, *i. e.*, about 0.006 second. These processes follow a law such that $I^{-1/2}$ is in linear relation to the time.

(8) The first and second processes, counting from the close of excitation, are of nearly equal duration, increasing in duration with the intensity of excitation in such a manner that the duration of the process is approximately proportional to the natural logarithm of the excitation.

(9) In certain salts, such as uranyl ammonium nitrate, decay is retarded by cooling; in other cases the temperature effect is slight.

(10) Uranyl nitrates with 2, 3, and 6 molecules of water of crystallization vary greatly in the rate of decay, but the changes in crystalline form appear to be more important in this respect than the amount of water.

(11) In the case of the polarized spectra of the double chlorides, both components decay at the same rate and no change in relative brightness can be detected throughout the range covered by observation.

PHOSPHORESCENCE OF LONG DURATION.

While comparing the spectra of uranyl salts under excitation by kathode rays and under photo-excitation, in 1917, Misses Wick and McDowell discovered that certain salts continued to glow for several minutes after bombardment in the vacuum tube, at the temperature of liquid air.

Many uranyl compounds are unstable in vacuo, and of those which are not decomposed rapidly, some, notably the chlorides, are practically inactive under the kathode rays. The following salts, which were prepared by Mr. Wilber in the form of fairly large, well-formed crystals, gave bright fluorescence and were fairly stable:

Uranyl potassium nitrate, $K_2UO_2(NO_3)_4$ (crystallized from 10 to 30 per cent nitric acid).
Uranyl potassium nitrate, $K_2UO_2(NO_3)_4$ (long crystals from 2 to 3 per cent nitric acid).
Uranyl potassium nitrate, $KUO_2(NO_3)_3$ (water form).
Uranyl potassium nitrate, $KUO_2(NO_3)_3$ (anhydrous).
Uranyl potassium sulphate.
Uranyl potassium sulphate (with 2 molecules of water).

An examination was made of all of this group. They were found to exhibit phosphorescence in varying degree. Some showed no phosphorescence of noticeable duration. The following, which were among the brightest, were selected for study:

(1 and 2) $K_2UO_2(NO_3)_4$. The first form, *A*, was crystallized from a 10 to 30 per cent solution of nitric acid, and the second form, *B*, from a 2 to 3 per cent solution. Although the crystallographic form is identical, form *A* crystallizes in short, thick crystals and form *B* in long, slender crystals. There appeared to be a slight difference in the phosphorescence of the two forms. It is possible, however, that the difference observed might have been due to some variation in the conditions under which the phosphorescence was produced.

(3) $K_2UO_2(SO_4)_2$. To ascertain whether, as the result of exposure to the kathode rays, the surface layer of the crystals had undergone some change which rendered them capable of persistent phosphorescence under photo-excitation, they were alternately illuminated by the light of a carbon arc and bombarded by the kathode rays. To accom-

plish this without changing any conditions except the mode of excitation the tube containing the crystal under observation was mounted within an unsilvered cylindrical Dewar flask and cooled to the temperature of liquid air. Light from a carbon arc was focussed upon the crystal through the walls of the Dewar flask and of the vacuum-tube, producing intense fluorescence, but there was no after-glow of duration sufficient to be detected. The kathode discharge, however, caused the persistent phosphorescence already described and the effect appeared to be distinctly cumulative, requiring excitation for several seconds. After the phosphorescence had died away, photo-excitation was resumed, and this process was repeated many times without observable change in the effect of the light.

IDENTITY OF THE SPECTRA DURING FLUORESCENCE AND KATHODE-PHOSPHORESCENCE.

To determine whether the spectrum, during this persistent phosphorescence, corresponded with the fluorescence spectrum, settings on several of the brightest bands were made with the Hilger spectroscope. The result was the same as the observations upon the brief phosphorescence following photo-excitation, described in an earlier paragraph of this chapter; *i. e.*, the spectra were found to be identical during and after excitation and remained unchanged in character as long as they were visible.

CURVES OF DECAY FOR THE KATHODE-PHOSPHORESCENCE.

Misses Wick and McDowell also determined the law of decay for the three salts (1, 2, and 3) selected for investigation. Since the effect lasted for several minutes, it was possible to use the method commonly employed in such measurements. The arrangement of the apparatus is shown in figure 44.

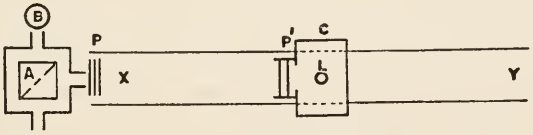

FIG. 44.

A Lummer-Brodhun cube A was placed at one end of a track XY, about 3.5 meters long. The crystal B was placed opposite one face of the cube. The comparison source L was a 5-volt tungsten lamp placed in parallel with a suitable rheostat upon a 55-volt circuit. The lamp was mounted in a carriage C, running on the track XY, on which, at intervals of about 25 cm., stops were placed. Green, blue, and ground glass absorption plates P and P' were inserted to obtain a comparison source of the proper color and intensity. A chronograph was used to record the time. The zero of time was in every instance recorded when the primary circuit of the induction coil was broken. When the

intensity of phosphorescence matched that of the source in the first possible position, the time was again recorded and the carriage moved to the next stop, and allowed to remain until a match was made as before. This procedure was continued until the phosphorescence was too faint to observe or until the end of the track was reached.

The interpretation of the results was somewhat difficult, since the instability of the crystals rendered uncertain both the control of the vacuum and the maintenance of the crystal surface unchanged during prolonged bombardment. The general shape of the decay curve after long excitation is shown in figure 45. The curves are of the type usual with phosphorescence of long duration, consisting of two linear processes, of which the first is the more rapid, whereas, as has been shown in the previous portions of this chapter, the decay following photo-excitation is of a new and entirely different type.

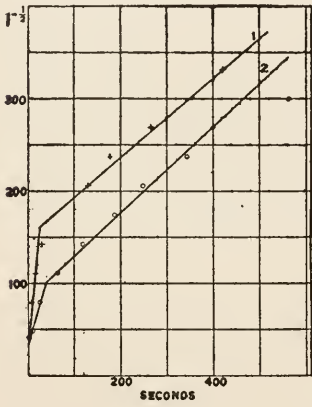

Fig. 45.

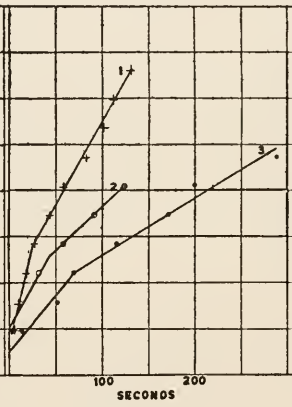

Fig. 46.

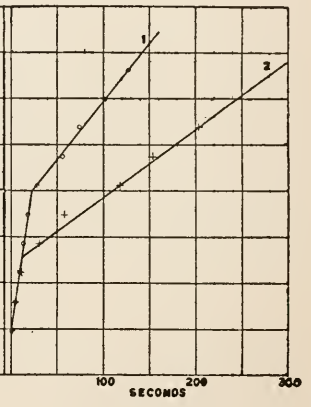

Fig. 47.

Under different conditions, phosphorescence was observed to last from less than a minute to 10 or 15 minutes. The exact form of the curve varied with the time of excitation. The time of decay was found to increase with the time of excitation, as shown in figure 46, but the initial brightness changed relatively little. There was some evidence to indicate that under similar conditions of vacuum the rate of the first process remained practically unchanged for varying times of excitation, but that the second process began sooner for longer excitation, as shown in figures 47 and 48. In figure 48, curves 1 and 2, obtained by a short-time excitation, show only the first process, whereas curves 45 and 46, obtained by excitations of 40 and 80 seconds respectively, indicate that a state of saturation had been reached such that added excitation produced no change in the phosphorescence.

As has been stated, the initial brightness and rate of decay were found also to depend upon the strength of the bombardment, as varied by the pressure in the tube and by the voltage applied to the induction

coil. The curves of figure 45, for example, were obtained with a relatively high vacuum, whereas those of figure 49 were obtained with a very low vacuum, so that the decay was comparatively rapid and there was only a suggestion of the beginning of the second process in the position of the last point observed. Slight changes in temperature, such as were produced when the liquid air fell below the line of the crystal, were found also to produce changes in the initial brightness and rate of decay.

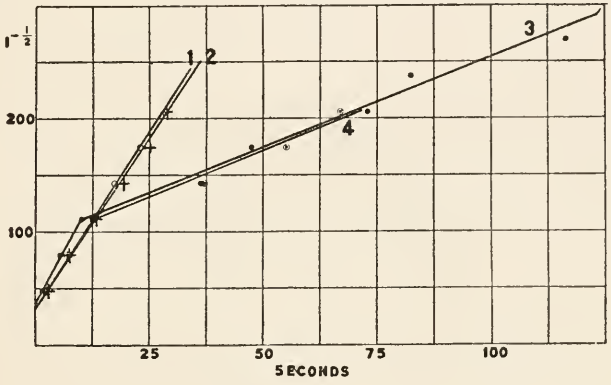

FIG. 48.

To determine whether the excitation produced any secondary change in the crystal, which persisted after the phosphorescence had disappeared, so that there would be a progressive building up of the phosphorescence, excitations were made of equal length, repeated at as nearly equal intervals as decay observations permitted. Figure 49 shows that, at a fairly low cathode vacuum, an excitation of 20 seconds, repeated at approximately 1-minute intervals, produced identical

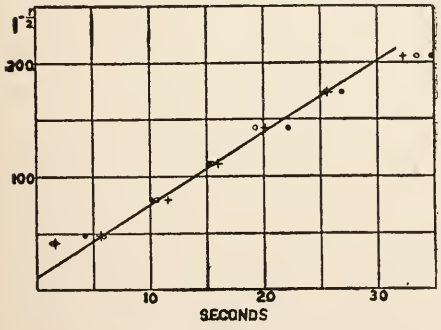

FIG. 49.

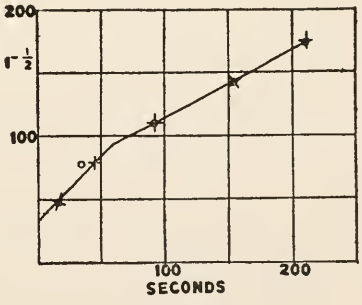

FIG. 50.

decay curves. The same effect is shown in figure 50 for a much longer period of decay. When the time between excitations was short as compared to the time and strength of excitation, there appeared to be a progressive change, as indicated in figure 51.

From this investigation by Misses Wick and McDowell, two definite conclusions may be drawn:

(1) The spectrum of the long-time phosphorescence produced by cathode-ray excitation at liquid-air temperatures is identical with the fluorescence spectrum.

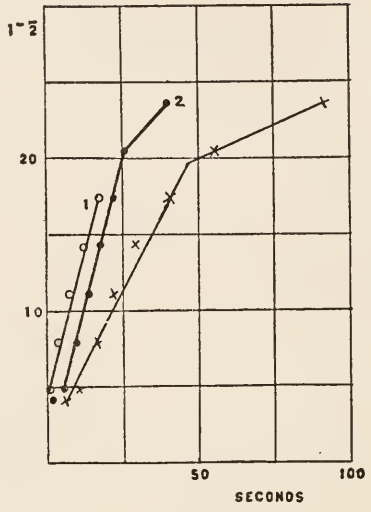

FIG. 51.

(2) The decay curve of the cathode phosphorescence differs in the most striking manner from that of the brief photo-phosphorescence. It corresponds in type with that usually found in cases of phosphorescence of long duration.

V. THE MORE INTIMATE STRUCTURE OF URANYL SPECTRA AS REVEALED BY COOLING.

It was first shown by J. and H. Becquerel and Onnes,[1] who studied the spectra of several of the uranyl salts when excited to fluorescence at the temperature of liquid air and ultimately at that of liquid hydrogen, that each band of the spectrum as we know it at $+20°$ is resolved into a group of much narrower bands. It was further shown by these investigators that all of the various groups of bands in a given spectrum were resolved in precisely the same manner, the homologous components forming series.

This more intimate structure, which is revealed by cooling, may be studied to great advantage in the case of the double chlorides, which salts, as has been noted in Chapter III, have spectra sufficiently resolved at $+20°$ so that the origin of the components observed at $-185°$ can be traced and the relation of the two spectra to one another much more definitely determined than is the case where the spectrum at $+20°$ consists of unresolved bands.

Four of these chlorides have the following composition:

$UO_2Cl_2.2KCl+2H_2O.$	$UO_2Cl_2.2RbCl+2H_2O.$
$UO_2Cl_2.2NH_4Cl+2H_2O.$	$UO_2Cl_2.2CsCl.$

They crystallize in triclinic plates which are strongly fluorescent and their spectra, which are almost identical in structure, are resolved at room temperature into 8 groups of narrow bands. Each group, which corresponds to a single band of the ordinary uranyl fluorescence spectrum, consists of 5 nearly equidistant bands. The symmetry of these spectra, as they appear to the eye when viewed with a spectroscope of moderate dispersion, is most striking. The bands are well separated from their neighbors and are about one-tenth as wide as the bands of the ordinary type of uranyl spectra.

The distribution of intensities within the group has been determined for the visually brightest group in the spectrum of the ammonium uranyl chloride by means of the spectrophotometer. The results of such a determination are given in table 18, and are shown graphically in figure 52.

The curve (fig. 52) which forms an envelope of the group of bands is of the same type as that for the distribution of intensities in a single band of the ordinary uranyl fluorescence spectrum and of the envelope of the set of bands in such a spectrum and is also similar to curves of distribution of the fluorescent spectra having a single broad band.[2]

The effect of cooling is likewise analogous, the envelope for $-185°$ being narrower on account of the great relative reduction in brightness of the outlying members of the group. All the bands are shifted in

[1] Becquerel and Onnes, Leiden Communications, 110. 1909.
[2] See Chapters II and III.

position as well as changed in intensity in a manner to be described in a subsequent paragraph.

To determine as closely as possible the wave-lengths of the bands, photographs of the spectra of the four double chlorides were taken and many visual settings were made. Fluorescence was excited by means of the carbon arc, the light from which passed through a screen opaque to rays of wave-length greater than about 0.45 μ and was focussed upon the crystal. Various exposures were employed on account of the great d fferences in the intensity of the bands and special plates were used for the red end of the spectrum. The exciting light was excluded from the camera by the use of suitable screens opaque to the blue and violet except where the absorption spectrum was to be recorded.

TABLE 18.—*Intensities of bands in group 6 (excited at +20° C).*

Band.	Intensity.
5306μ	18
5259	33
5208	24
5159	11
5119	(1)

[1] Visible, but too dim for spectrophotometric measurement.

The various negatives were measured by mounting them on a micrometer stage in the field of the lantern. The micrometer-screw was carefully calibrated, so that wave-lengths could be determined by measuring the distance of the crests of the bands from certain reference lines of the mercury spectrum, which was photographed on each negative so as to overlap the fluorescence spectrum.

This method of projection was found better than the use of the comparator commonly employed in the measurement of line spectra, because of the hazy character of the bands and because bands that are so weak and vague as to be invisible even under a low-power microscope could be seen and located by means of the lantern. Many measurements of the stronger bands were made with the comparator as a check on the determinations with the lantern.

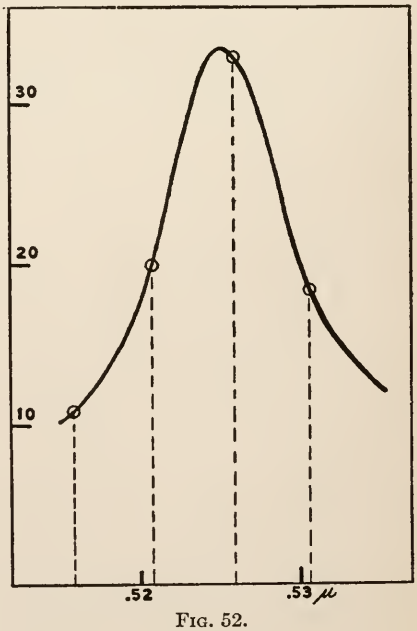

FIG. 52.

These measurements confirmed to a remarkable degree the apparent symmetry of the spectrum. When all the bands are plotted on a large scale, in a diagram with the reciprocal of wave-lengths as abscissæ, the spectrum is seen to consist of 8 groups of 5 bands each, as already described. The nearly uniform arrangement of the bands of each group repeats itself precisely from group to group, so that corresponding members of the groups form an

homologous series of equidistant bands. This interval, moreover, is very nearly the same for all five of these homologous series; but although the departures from equality are of the same order as the errors of measurement, there is reason, as will be seen later, to regard them as real.

The general arrangement of the bands in these spectra is roughly depicted in figure 53, which is based upon measurements of the fluorescence spectrum of the ammonium uranyl chloride. Horizontal distances are plotted on the scale of frequencies, the corresponding wave-

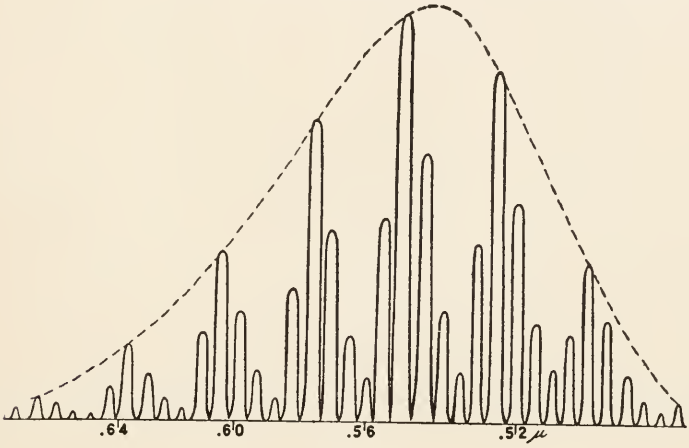

FIG. 53.

lengths being indicated for convenience. Vertical heights indicate relative intensities, but with some pretence of accuracy. The first and eighth groups at the extreme left and right, for example, if drawn to scale, would be scarcely visible. They are, in fact, so feeble that they can be observed only with the greatest difficulty. The location of the various bands of the 4 double chlorides, in wave-lengths and in frequencies ($1/\mu \times 10^3$) is given in table 29 at the end of this chapter. The values given are the averages of several readings from the photographs and from visual settings. The bands in each group from the red toward the violet are designated by the letters *B*, *C*, *D*, *E*, and *A*, and bands having the same letter thus form homologous series.

To determine the intervals between groups, the position of what may be called the center of each group was found by averaging the frequencies of all 5 bands. The intervals between these centers for groups 2, 3, 4, 5, 6, and 7 are given in table 19. Groups 1 and 8, for which insufficient data were available, were omitted, except in the case of the ammonium chloride.

The only indication of a systematic departure from uniformity of interval for a single salt appears in the case of the cæsium chloride, the average group-interval for which is smaller than that of the other salts by nearly 0.5 per cent.

As will appear in the course of the subsequent consideration of individual series, the tendency of the group intervals of the cæsium salt to diminish toward the violet is not, as might seem at first sight, an indication that the groups are made up of series having a diminishing interval. As regards the other salts, it will be noted that the *distance between groups is essentially constant.*

TABLE 19.—*Distances between fluorescence groups.*

Group.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	Center of group.	Interval.	Center of group.	Interval.	Center of group.	Interval.	Center of group.	Interval.
1	.....	.....	1505.3	.....	.....	.....	.....	.....
2	1587.2	.....	1588.6	83.3	1591.5	.....	1592.6	.....
3	1670.8	83.6	1671.9	83.3	1674.9	83.4	1675.9	83.3
4	1754.0	83.2	1755.0	83.1	1758.3	83.4	1759.3	83.4
5	1836.6	82.6	1838.4	83.4	1840.7	82.4	1841.8	82.5
6	1919.6	83.0	1922.3	83.9	1924.2	83.5	1924.7	82.9
7	2003.3	83.7	2005.6	83.3	2007.8	83.6	2006.6	81.9
Average distances		83.22	.....	83.38	.....	83.26	.....	82.80

DISTRIBUTION OF BANDS WITHIN THE GROUPS.

While to the eye the fluorescence spectra under consideration present the appearance of evenly spaced bands varying periodically in intensity so as to form the groups, this is not strictly the case, as may readily be shown by subtracting neighboring values in table 29. The average distances thus obtained are given, for convenience, in table 20.

The greatest departures from uniformity of distribution occur in the spectra of the rubidium chloride and the cæsium chloride.

TABLE 20.—*Average distances between neighboring bands in the fluorescence spectrum at +20° C.*

Fluorescing substances.	Distances between bands.				
	C to B.	D to C.	E to D.	A to E.	B to A.
$UO_2Cl_2.2KCl$	15.97	18.66	17.96	14.70	15.58
$UO_2Cl_2.2NH_4Cl$	17.56	17.74	17.86	15.67	15.67
$UO_2Cl_2.2RbCl$	16.20	18.43	18.50	12.75	17.12
$UO_2Cl_2.2CsCl$	18.25	12.85	18.63	14.52	18.10
Averages	16.99	16.92	18.24	14.41	16.62

In the rubidium spectrum, bands A and E are crowded together, the average interval being 12.75, and in the cæsium spectrum D and C are similarly crowded. It will be noted that the average distance between A and E is less for the four chlorides than any of the corresponding distances between other bands.

The arrangement of the bands within the group in the four salts is conveniently compared by means of the diagram in figure 54, in which

the geometrical centers of the groups are in the same vertical line. It will be seen from the diagram:

(1) That the group center is in all four cases almost coincident with the crest of the D band.

(2) That the distance between D and E is approximately the same in all.

(3) That the arrangement of bands within the group is essentially the same in all, except for the displacement of band A in the spectrum of the rubidium and of B and C in that of the cæsium salt, as mentioned above.

Further discussion of these discrepancies will be found in a later paragraph of this chapter.

INTERVALS OF THE INDIVIDUAL SERIES.

For the consideration of the frequency intervals of the individual series, the values from table 29 have been arranged by series in table 30. Distances between the observed positions of neighboring members of each series are given in the column marked "Intervals." To facilitate the detection of systematic departures from uniformity of interval, a column of values calculated by the following method is likewise given: A "center" for each group was found in the manner already employed for determining the group centers. Around this the calculated positions were arranged under the assumption of a constant frequency interval equal to the average of the observed intervals for each series separately. The column marked "Differences" indicates the departure of the observed values from those thus calculated. The departures from uniformity of interval are unsystematic, indicating, *for all the salts, that the series may be regarded as having a constant frequency interval.*

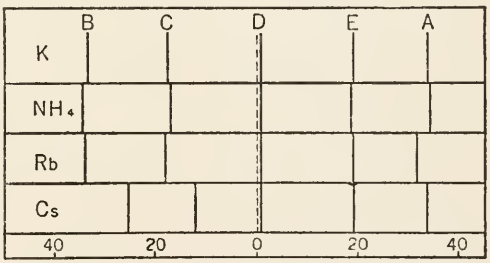

FIG. 54.

This interval has been computed for each series by subtracting the *observed* frequency of each band from the frequencies of all the other bands of the series and dividing the sum by the total number of intervals in question. The results are presented in table 21.

These data indicate no progressive change of interval with the molecular weight, except that the interval is definitely smaller for the cæsium uranyl chloride. The other three salts, so far as this determination goes, must be regarded as having the same average interval. It is likewise difficult to distinguish with certainty differences in the intervals of different bands in a given salt, except that the C band has in general a smaller interval than the other series, or of a given band in the different salts, excepting in the case of the cæsium chloride.

At the same time, while not obviously systematic, the variations in these values are considerably larger than those resulting from the measurement of the interval of any given series, taken by itself, which should not exceed, at most, 0.2.

TABLE 21.—*Average intervals at +20° C. for the four double chlorides.*

Series.	K.	NH_4.	Rb.	Cs.	Av. by series.
B.....	83.42	83.34	83.49	82.32	83.14
C.....	83.11	82.99	82.97	82.50	82.89
D.....	83.30	83.21	83.17	82.85	83.13
E.....	83.00	83.81	82.97	83.45	83.31
A.....	83.23	83.65	83.77	82.85	83.37
Av...	83.21	83.40	83.27	82.80	83.17

These seeming discrepancies are not to be considered as wholly accidental, but as being due to the fact that the bands are complex, and variously so, as will appear from the study of these spectra at low temperatures.

While he determinations thus far described may be regarded as indecisive as to small differences of *interval* between the various series and salts, excepting as noted above, the influence of molecular weight upon the *position* of bands in the spectrum is unmistakable.

In tables 29 and 30 (at end of chapter) the almost universal and fairly regular increase in the frequency of each band as we pass from potassium to cæsium is sufficiently evident. In figure 55 this general shift, which is present in all the groups and affects all series, can be seen at a glance. Almost the only reversed shifts occur in the case of those bands of the cæsium spectrum which show anomolous placing in the spectral groups.

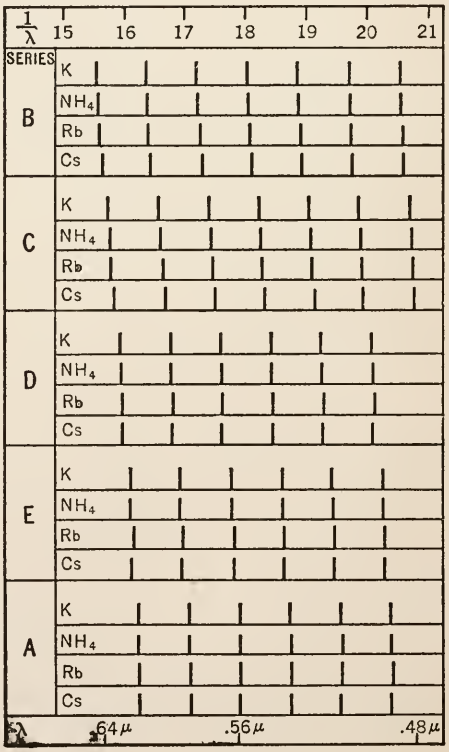

FIG. 55.

In table 19, where the groups are units, the accidental errors pertaining to individual bands are submerged in the processes of averaging and the shift with molecular weight appears as a still more

systematic phenomenon. Ignoring group 7, in which the bands are displaced by absorption in a manner to be discussed later, we find the following shifts to exist.

TABLE 22.—*Shift of the groups.*

Group.....	2	3	4	5	6
Shift.....	5.4	5.1	5.3	5.2	5.1

Average shift from K to Cs, 5.2

Ths shift is therefore to be regarded as *approximately uniform throughout the spectrum.* The shift is much greater between NH_4 and Rb than in the other cases, the averages being as shown in table 23.

TABLE 23.—*Average shift of groups.*

K–NH_4.....	1.6
NH_4–Rb.....	2.7
Rb–Cs.....	.9

It will be noticed that in this discussion the order of molecular weights used is K, NH_4, Rb, Cs—NH_4 being placed between K and Rb instead of in its proper position. This is in accordance with the results of Tutton,[1] who has shown that in various optical properties of crystals which depend on the molecular weights, NH_4 always lies between K and Rb, as though its effective molecular weight were larger instead of being smaller than K.

THE EFFECTS OF TEMPERATURE.

The narrow, line-like bands into which the ordinary uranyl spectrum is resolved at low temperatures[2] form a rather complex aggregation separable into a series of identically arranged groups corresponding to the unresolved bands at +20°, but related to the overlapping components of the latter in a manner not easily capable of direct determination. It was deemed of especial interest, therefore, to observe the effect of cooling on the double chlorides, where the relation, owing to the partial resolution at +20°, should be more obvious.

For this purpose a crystal, *C*, of the salt to be examined was mounted within a long cylindrical Dewar flask, *D*, with unsilvered walls (fig. 56). The carbon arc *A* was focussed on the crystal by the lens *L*. A water-cell *W* was inserted between the arc and the condenser. The light-filter *F* was opaque to all but the violet and ultra-violet rays used for excitation. Observations with the Hilger spectroscope *H*, a portion of the collimator of which is shown, were made through a second filter *E* opaque to the exciting light but transmitting the fluorescence. The arc and specimen were well screened by an opaque box *BB*. When it was desired to photograph the spectrum a camera was substituted for the observing telescope of the spectrometer.

The control and adjustment of temperature were effected by attaching the crystal at the upper end of a vertical copper rod which could be

[1] Tutton, A. E., Crystalline Structure and Chemical Constitution. (London, 1916.)
[2] See Becquerel and Onnes, l. c.

immersed more or less deeply in the liquid air by raising or lowering the Dewar flask. To preclude the gathering of frost or moisture on the surface of the crystal, it was kept during the entire experiment at a sufficient distance below the lip of the flask, where it was surrounded with the dry atmosphere above the slowly evaporating mass of liquid air. Measurements of the temperature were by means of a small coil of fine copper wire mounted at the same level as the crystal, so as to have always, as nearly as possible, the temperature of the latter. Changes in the resistance of the coil were indicated on the sheet of a Callender recorder, carefully calibrated to read directly in degrees centigrade and adjusted for a range from $+20°$ to $-200°$.

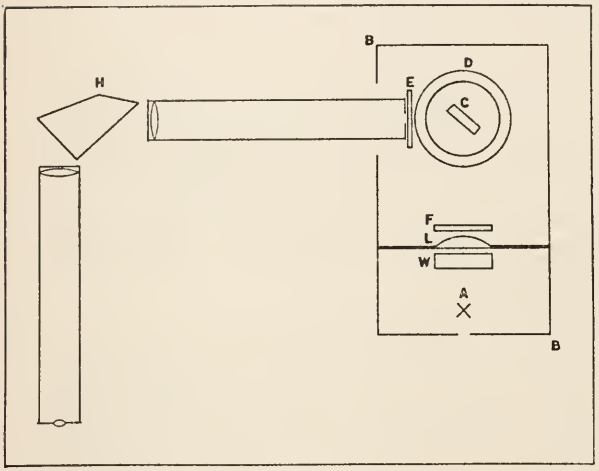

Fig. 56.

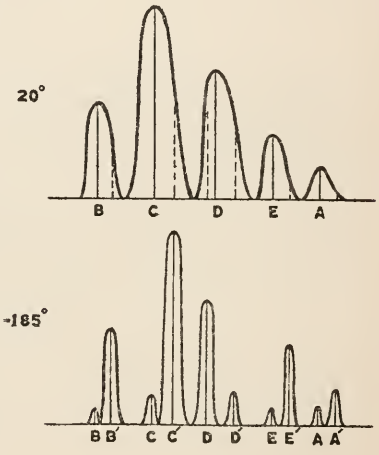

Fig. 57.

The crystal was mounted so as to cover a transverse slot in the copper rod. It could thus be illuminated either from the front, as shown above, or from behind by light transmitted through the slot. The latter arrangement was employed especially in the study of the absorption spectrum.

When the substance, excited to fluorescence in the manner already described, was gradually cooled to the temperature of liquid air and the spectrum was observed through the Hilger spectrometer, the following changes were noted:

(1) The bands become narrower and better defined until at the temperature of liquid air they correspond in appearance to the usual line-like bands characteristic of the fluorescence spectra of the uranyl salts at low temperatures.

(2) As the temperature falls the bands are gradually resolved into doublets. One component of each doublet becomes rapidly brighter, while the other frequently becomes more indistinct and sometimes disappears. The general effect is that of a shift toward the violet

amounting to about a third of the distance between the original bands. The nature of this apparent shift is as follows:

Each band at +20° may be regarded as an unresolved doublet, of which in general the member of longer wave-length is relatively so much the stronger that its position determines approximately the location of the crest of the composite band (see fig. 57). The effect of cooling is to resolve this doublet into separately distinguishable bands and at the same time to cause a subsidence of the stronger and an increase of the weaker member. The member of the shorter wave-length usually becomes dominant at low temperatures, and in so far as this occurs the arrangement of the spectrum appears to be undisturbed but shifted toward the violet by an amount representing the width of the doublet. There are, however, certain exceptions to this rule, so that the relation of the resolved spectrum to that at +20° is not so simple as the above description would imply. The appearance of the group, if this be its real structure (*i. e.*, a set of nearly equidistant doublets, the distance between the members of all the doublets being nearly the same), would then be as shown in figure 57.

At +20°, B', C', D', E', and A' are entirely concealed by the overlapping of the bands. At −185°, B, C, D', E, and A may or may not be visible, according to their intensity or the completeness of the resolution, which in fact varies greatly in different parts of the spectrum.

It will be noticed that in the lower diagram in figure 57, D and not D' is the dominant component. This is a condition which obtains in the ammonium chloride, with the result that C' and D, which appear to have replaced the strong C and D bands of the spectrum of +20°, are near together, D and E' far apart, and the symmetry of the group is impaired. Similar complications occur likewise in the spectra of the other double chlorides.

To illustrate the application of this assumption, the spectrum of the ammonium uranyl chloride has been mapped in the manner shown in figure 58, in which the fluorescence bands of the 8 groups as they occur at −185° are shown in their relation to a hypothetical grouping given at the head of the diagram. This grouping consists of the set of imagined doublets of which, as in a previous paragraph, the spectrum at +20° is supposed to be made up. The spacing for each doublet is that determined from the observed average shift on cooling and the relative divergence from this arrangement is shown for all the bands of each group.

A scrutiny of the fluorescence spectrum at −185°, group by group, by means of this diagram, affords very satisfactory confirmation of this hypothesis concerning the apparent shift. It is obvious:

(1) That not all the components B, C, D, E, and A will necessarily be visible in every group of the resolved spectrum.

(2) That lack of resolution in any region may give the appearance of a single band with intermediate crest in place of the doublet.

(3) That the position of crests of the unresolved doublets at +20° will not necessarily coincide exactly with that of either component.

Bearing these points in mind, it will be seen that were resolution complete all the observed bands of the spectrum at −185° would probably fall into the system proposed above.

We may imagine that the difference between the resolution of the bands *C* and *D*, for example, as seen in figure 54, is produced by changes in the unresolved doublets at +20° when the temperature is reduced to −185°, of the kind indicated in figure 59. The doublet *CC′* forms a single band with crest nearly coincident with *C* at +20°, and this owing to the subsidence of *C* and growth of *C′* takes the resolved form shown at −185°. In the case of *D*, however, the unresolved band has an intermediate crest at *D*, but is really composed of overlapping components *D′* and *D″* which are separately visible at −185°.

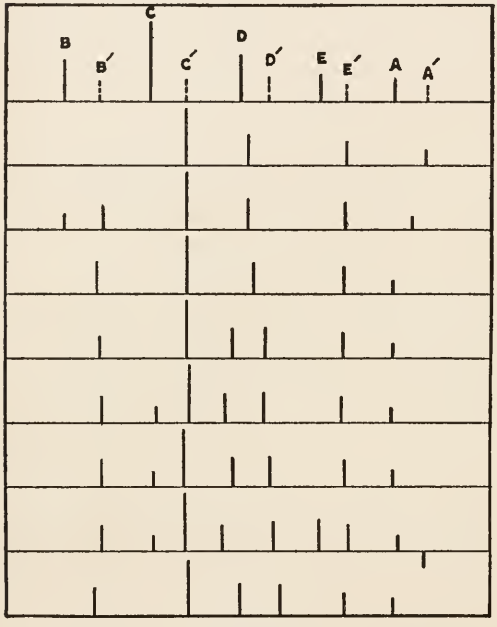

Fig. 58.

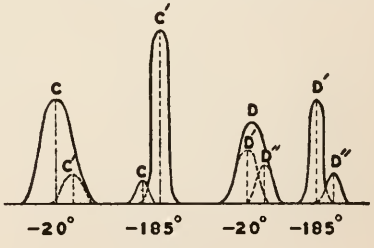

Fig. 59.

The wave-lengths and frequencies of the bands in the resolved spectra of the four double chlorides, as observed when excited at the temperature of liquid air, are given in table 31 at the end of the chapter. The nomenclature used in this and subsequent tables is chosen to indicate as far as possible the relation of the bands at −185° to those at +20°. Thus B_1, B_2, etc., denote components of *B*, etc., which have been rendered visible by the resolution effected by cooling.

The explanation offered above to account for the relation between the spectra at +20° and at −185°, and which was illustrated in the case of the ammonium uranyl chloride (see fig. 58), was confirmed by observations upon the spectrum of that salt at intermediate temperatures. It was thus possible to watch the gradual appearance of the

components characteristic of the spectrum at low temperatures and the simultaneous fading away of those dominant at +20°. The same explanation applies equally well to the potassium and rubidium double chlorides. In the case of cæsium uranyl chloride the relations are complicated by the further resolution of these components, so that the connection with the original complexes is less easily traced.

To indicate the general character of these resolutions and the apparent temperature shift which results therefrom, the positions of the bands of group 6 at −185° are plotted for all four chlorides (see fig. 60). Intensities of the −185° bands are indicated roughly by the height of the lines. The corresponding crests of the bands at +20° are represented by dotted lines. Group 6 was selected because it offers better examples of the further breaking-up of the components and of other phases of the process of resolution than do groups toward the red in which resolution is progressively less complete.

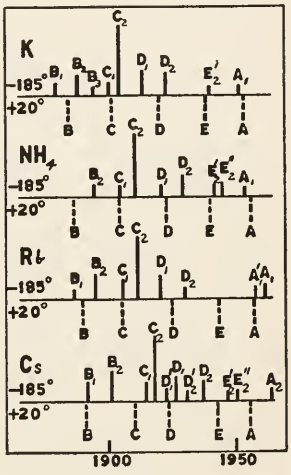

Fig. 60.

Two questions which were left undetermined in the study of the spectra at +20° may be regarded as settled by these measurements of the bands at −185°.

(1) That the intervals are not the same for all series in a given spectrum is clearly established. For example, the components C_1, C_2, which take the place of the C bands in all four spectra, have distinctly different intervals, *i. e.*, 84.00 for C_1 and 82.75 for C_2. It is noteworthy that C_2, which becomes the crest of the group in place of C also, has the small interval. It might be questioned whether these so-called components are not merely accidental neighbors rather than products of the same vibrating system, but for the fact that they are present in all the spectra and have very nearly if not precisely the same relative positions to each other in all.

(2) The average interval of all series in the spectrum of the cæsium chloride (82.80) at +20°, which causes the notable displacement of the bands of that substance, becomes 83.44 when we take the average of the intervals of the bands at −185°. That is to say, it is, within the errors of observation, the same as the general average for the other salts. On the basis of the measurements at low temperatures (see table 24), we must conclude that the four double chlorides have approximately the same average frequency interval.

The averages given in table 24 are obtained from the data of table 32, which contains the frequencies of all the fluorescence bands observed in the spectra of the four double chlorides when excited at the tempera-

ture of liquid air. As in the corresponding table for +20° (table 30) the arrangement is by series.

TABLE 24.—*Average intervals of the fluorescence series at −185° C.*

Series.	K.	NH_4.	Rb.	Cs.	Average.
B_1....	83.9	83.0	84.2	83.0	83.53
B_2....	83.1	83.2	83.6	83.4	83.33
B_3....	83.5	.....	.....	.....	.....
C_1....	84.9	84.1	84.0	83.7	84.18
C_2....	82.7	82.7	82.9	82.8	82.78
D_1....	83.1	83.8	83.6	83.1	83.40
D_1'...	.....	.....	.....	84.5	.....
D_2....	84.1	84.2	84.0	83.6	83.98
D_2'...	.....	.....	.....	83.6	.....
E_2'....	83.6	82.5	.....	83.2	83.10
E_2''...	.....	83.3	.....	83.5	83.40
A_1....	83.3	83.1	82.1	.....	82.83
A_2....	.....	.....	83.6	83.4	83.50
	83.58	83.32	83.50	83.44	.....

THE ABSORPTION SPECTRA.

A glance at the absorption spectra of the double chlorides, obtained by viewing through a spectroscope the light transmitted by the crystals at room temperature, shows the same higher degree of resolution that characterizes the fluorescence spectra of these salts. The salient feature is a series of strong, rather narrow bands, equally spaced as to frequency, like the broader bands of the other uranyl compounds. The interval, as in all uranyl absorption spectra, is distinctly smaller than the fluorescence interval. Between these are several series of weaker bands.

The complete mapping of the absorption spectra is difficult. It can not be done visually, since the bands extend out into the darkness of the ultra-violet. Photography adds considerable detail, but does not greatly extend the range toward the shorter wave-lengths on account of the rapidly increasing opacity. In the brighter regions of the spectrum, on the other hand, more can be seen with the eye than can be found on the photographic plate. The data which we have obtained and which are presented in the tables at the end of this chapter have been procured by supplementing the photographic method, wherever desirable, by visual observations.

A great variety of light-filters and combinations of light-filters have been employed in different parts of the spectrum, with widely different exposures for the strong and weak bands. The thickness of the transmitting layer has likewise been varied as far as the available material would permit. We are convinced, however, that the extreme limits of the absorption, in both directions, have not as yet been reached.

By using crystals of unusual thickness, especially prepared for this work and sometimes by mounting several crystals one behind the

other, so as to greatly increase the depth of the transmitting substance, it has been found possible[1] to greatly extend the absorption spectrum toward the red.

Since the crystals are of a greenish-yellow color, they become rapidly transparent as the light admitted is changed from blue to yellow; hence the use of increasingly thicker layers to bring out the absorption bands. To a certain extent the crystal acts as a screen to absorb the blue light which would cause fluorescence; nevertheless it was found necessary to interpose orange or yellow screens of different densities to eliminate fluorescence in a region where ordinarily it is at a maximum. At first colored glasses obtained from Dr. H. P. Gage, of the Corning Glass Company, were used as filters; later, solutions of potassium bichromate of varying concentration. It is evident that the screening must be constantly changed when light from the arc is used as a background for bands of increasingly longer wave-length. It was thought that a beam of monochromatic light could be used as a background and thus obviate exciting the crystal to fluorescence, but a preliminary study indicated that such a beam of dispersed light could not be made of sufficient intensity to bring out the dimmer bands.

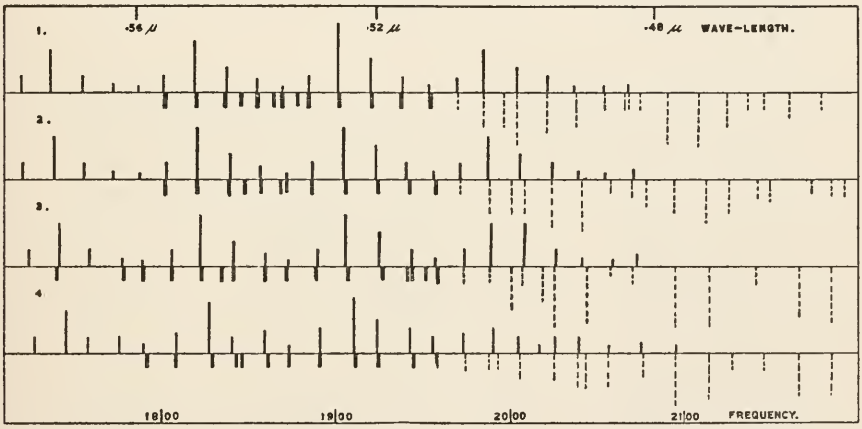

FIG. 61.—Fluorescence bands are indicated by lines *above* the horizontal. Old absorption bands are indicated by dotted bands *below* the line; new absorption bands by *solid* bands below the horizontal. The plot shows only a portion of the complete spectra of the following salts at +30° C: (1) potassium uranyl chloride; (2) ammonium uranyl chloride; (3) rubidium uranyl chloride; (4) cæsium uranyl chloride.

In figure 61 is pictured a portion of the fluorescence and absorption spectrum of each of the double chlorides studied. Fluorescence bands are designated by lines above the horizontal line. The older, well-established absorption bands are designated by dotted lines below the horizontal and the new bands by solid lines below the horizontal. The relative positions of the fluorescence and absorption bands are readily seen. These bands appear to be of two distinct classes:

[1] Howes, H. L., Physical Review (2), XI, p. 66. 1918.

(1) Most of them at +20°, as may be seen from the diagram and from table 25, in which they are listed together with the corresponding fluorescence, are reversals of fluorescence. These do not form a continuation of the absorption series lying farther toward the violet, nor can they be grouped in series having the absorption interval of 71±. In all four species every fluorescence band of groups 5 and 6 has its

TABLE 25.—*New absorption bands at +20° C.*

Potassium uranyl chloride.				Ammonium uranyl chloride.			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1802.1	1801.4	B	.....	1802.5	1803.1	B	.....
1820.2	1819.3	C	.....	1820.8	1820.7	C	.....
1836.5	1837.6	D	.....	1838.9	1839.7	D	.....
1846.0	.....	.....	*c*	1848.8	.....	.....	*c*
1855.3	1855.3	E	.....	1857.8	1856.9	E	.....
1865.0	.....	.....	*d*	1869.2	.....	.....	*d''*
1869.4	1869.6	A	.....	1871.8	1871.8	A	.....
1879.0	.....	.....	*e*	1886.5	1886.8	B	.....
1885.1	1884.7	B	.....	1906.2	1904.6	C	.....
1902.2	1901.5	C	.....	1924.2	1923.2	D	.....
1920.9	1920.1	D	.....	1942.3	1940.5	E	.....
1937.6	1938.3	E	.....	1957.4	1956.3	A	.....
1954.7	1953.5	A	.....				
Rubidium uranyl chloride.				**Cæsium uranyl chloride.**			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1740.0	1741.6	C	.....	1791.5	1789.7	A	.....
1778.7	1777.8	E	.....	1808.0	1808.6	B	.....
1789.5	1789.4	A	.....	1829.2	1827.5	C	.....
1806.1	1806.1	B	.....	1843.0	1840.5	D	.....
1823.2	1822.8	C	.....	1846.4	.....	.....	*β*
1834.9	.....	.....	*b*	1861.2	1859.1	E	.....
1841.6	1841.5	D	.....	1873.0	1873.1	A	.....
1859.8	1859.8	E	.....	1890.7	1891.1	B	.....
1872.0	1873.1	A	.....	1911.1	1910.4	C	.....
1889.0	1890.0	B	.....	1923.8	1923.6	D	.....
1907.2	1905.5	C	.....	1944.4	1942.7	E	.....
1926.7	1925.0	D	.....	1957.8	1955.7	A	.....
1941.7?	.....	.....	*d*				
1944.0	1943.5	E	.....				
1952.0?	.....	.....	*e*?				
1958.7	1957.1	A	.....				

corresponding absorption band, and this relation extends to some of the bands of group 4. Indeed, the suspicion would seem warranted that were the proper experimental conditions attainable throughout the spectrum, every fluorescence band would be found to have its related absorption band and to be reversible in the sense in which that term is defined in a subsequent paragraph.

(2) The remaining bands listed in table 25 are not reversals of fluorescence. They belong to existent absorption series, of which they are the members of greatest wave-length as yet observed.

It should be noted that special precautions were taken to avoid bias. They were not sought for by locating the fluorescence bands and looking for reversals, but found under conditions of illumination which

TABLE 26.—*New absorption bands at −185° C.*

Potassium uranyl chloride.				Ammonium uranyl chloride.			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1941.7	1940.0	E_2'	d_2	1945.9	1945.0	E_2''	d_2''
1947.6	.....	.....	e_1	1953.5	1953.7	A_1	e_1
1954.7	.....	.....	e_2'	1956.6	.....	.....	.....
1960.4	.....	.....	b_1'	1963.5	.....	.....	e_2''
1965.8	1963.9	B_1	a_1	1967.7	1968.7	B_1	b_1
1972.4	1972.3	B_2	b_2	1973.6	.....	.....	b_2'
1977.5	1977.8	B_3	b_3	1977.1	1977.9	B_2	b_2
1984.9	.....	.....	c_2'	1981.0	.....	.....	b_2''
1989.3	.....	.....	c_2''	1984.9	.....	.....	b_3
1998.0	1997.2	D_1	d_1	1992.0	1992.7	C_2	c_2
2008.8	2007.4	D_2	d_2	1996.8	.....	.....	.....
				2002.8	.....	.....	d_1'
				2006.8	.....	.....	d_1''
				2014.1	.....	.....	d_2''
Rubidium uranyl chloride.				Cæsium uranyl chloride.			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1944.4	.....	.....	d_2''	1953.9	.....	.....	d_2''
1952.4	.....	.....	e_1'	1956.6	.....	.....	.....
1954.7	.....	.....	.....	1958.9	.....	.....	e_2'
1958.1	1957.9	A_1	e_2'	1967.0	.....	.....	a_1'
1963.9	.....	.....	a_1'	1970.8	.....	.....	.....
1973.9	.....	.....	b_1''	1974.3	.....	.....	b_1'
1981.0	.....	.....	b_2	1978.2	.....	.....	b_1''
1985.7	.....	.....	.....	1982.9	.....	.....	b_2'
1995.6	.....	.....	c_2	1987.7	.....	.....	b_2''
2005.2	2003.7	D_1	d_1	1991.3	.....	.....	b_3
2010.1	.....	.....	d_2'	1997.6	1997.6	C_1	c_1
2016.1	.....	.....	d_2''	2005.6	.....	.....	c_2
				2009.6	2008.5	D_1	d_1
				2016.1	2014.9	D_2'	d_2'
				2022.2	.....	.....	d_2''

rigorously excluded fluorescence, and in many instances their existence and place was checked by two observers working independently.

The fact that practically the entire group was in approximate coincidence with fluorescence was an unlooked for result of which we became aware only after the measurements had subsequently been plotted. The expectation was that these bands would prove to be members of the absorption series lying farther toward the violet.

A search by similar methods failed to reveal any bands of class (1), mentioned above, in the spectra of the crystals when cooled to the temperature of liquid air. No selective absorption could be detected beyond the violet end of group 6, $1/\lambda$ 1940, and while a considerable number of new absorption bands were detected, nearly all of these (see table 26) were found to be members of series already recognized. The exceptions, two each in the spectra of the ammonium, rubidium, and cæsium double chlorides, do not appear to be related to the fluorescence. Coincidences between fluorescence and absorption are of the sort already established as characteristic of the reversing region.

TABLE 27.—*Average intervals of absorption series at +20° C.*

Series.	K.	NH_4.	Rb.	Cs.	Av.
b.....	70.5	71.6	70.4	70.9	70.9
β.....	.....	.....	.....	70.6	.....
c.....	70.8	68.8	70.3	.....	70.0
γ.....	70.4	70.7	70.4	.....	70.5
d'.....	.....	.....	.....	70.9	.....
d.....	71.1	71.0	71.2	70.3	70.9
d''.....	70.6	70.3	.....	.....	70.5
e.....	70.0	69.7	70.8	70.6	70.3
e''.....	70.4	70.8	69.6	.....	70.3
a.....	.....	.....	.....	70.8	.....
a''.....	70.0	.....	69.3	.....	69.7
Av....	70.5	70.4	70.3	70.6	.....

The failure to find the bands in groups 5 and 6 is not surprising. They are sufficiently difficult objects at +20°, where two or more components are blended into a broader band. The existence of these components at −185° may be regarded as probable, but they were invisible under the conditions which we have thus far been able to obtain.

The absorption spectra of the double chlorides do not exhibit the same remarkable approach to identity of structure and regularity of arrangement manifested in the fluorescence spectra. Upon analysis, however, they are all found to consist of series having intervals of approximately 70 frequency units. As may be seen from table 27, this interval for a given series is very nearly the same for all four salts. The average interval for all the series of a given salt is constant within the errors of observation. These averages are based on the values in table 33 at the end of this chapter.

The absorption bands, unlike those of the fluorescence spectrum, do not appear to fall into a succession of strictly homologous groups, but this is because some series disappear, while others increase in strength

toward the violet. A group near the fluorescence region, therefore, differs notably in aspect from one in the extreme violet, and it is difficult to base conclusions on the location of the centers of the groups, as was done in the study of the fluorescence spectra.

As may be observed in figure 62, where the ninth group for the four spectra at +20° is plotted, the distances between the consecutive bands are less nearly equal than the distances between fluorescence bands. It is also evident from this figure that with increasing molecular weight there is a general shift toward the violet. The shift is apparently less systematic than with the fluorescence bands and several reverse shifts seem to occur. In general, however, the total displacement is approximately the same as that observed for fluorescence, *i. e.*, 5 frequency units from potassium to cæsium.

EFFECT OF TEMPERATURE ON THE ABSORPTION SPECTRA.

In the study of the absorption of the double chlorides at −185°, a modification of the method described in a previous paragraph in the investigation of the fluorescence at low temperatures was made. (See fig. 56.) The crystal under observation was mounted within a Dewar flask and submerged in liquid air. Light was transmitted through the crystal instead of being reflected from its surface and a nitrogen-filled tungsten lamp was, in general, substituted for the carbon arc. Both photographic and visual methods were tried, and in the reversing region, especially, where fluorescence and absorption overlap, much attention was given to the selection of color-screens to exclude fluorescence from the portion under consideration.

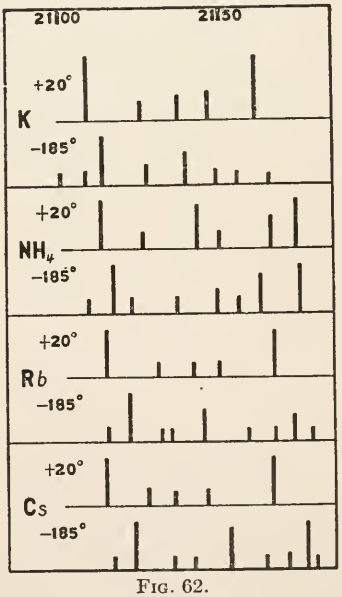

FIG. 62.

A complete list of the absorption bands observed at −185° will be found in table 34.

The three most obvious results of cooling to the temperature of liquid air are: (1) a general shift toward the violet; (2) a great increase in the number of bands; (3) a very decided narrowing and sharpening of the bands.

These changes are readily accounted for by the assumption already made, in this chapter, that the bands at +20° C. are concealed doublets and that the effect of cooling is to resolve them while simultaneously reducing the strength of the stronger and increasing the strength of the weaker component. The apparent shift thus produced will vary from zero to 5 or more units, according to the distance between the components.

A few bands at $-185°$ are so located with regard to the $+20°$ bands that to explain them by this theory we must suppose them to be too feeble at $+20°$ for detection and greatly increased in intensity by cooling.

There is also evidence in places of further resolution into closer narrow doublets and as the degree of resolution is not always the same with fluorescence and the corresponding absorption, this is a source of trouble in the attempt to find the fluorescence series which belongs to each series in the absorption spectrum. Every low-temperature band, however, falls into a series of constant frequency, whatever its position or degree of resolution.

The effect of temperature on the average intervals can be studied by comparing tables 27 and 28. Although the intervals range from 69 to 71, there is little that can be termed systematic in the variations.

At liquid air temperature, where two or more components are present, we have used subscripts. Thus d_1, corresponds to D_1, d_2 to D_2, etc. Where the reversal is doubled in the manner shown in figure 63, we have designated this doublet as d_1' and d_1'', etc.

The average interval of each salt is approximately the same at both temperatures. It will be noticed in table 27 that 70.28, the average of the *c* components is smaller than the *b*, *d*, *e*, or *a* averages. This is of interest because the strong C series, which join these series, are also the shortest of the fluorescence series. Since the $-185°$ bands are very sharp and easy to locate, no doubt the differences found in table 28 are indicative of real variations in the constant-frequency intervals. It does not follow that the smaller intervals are confined to one salt or one set of bands, however, since, as has been noted in the case of series C_1 and C_2 of the fluorescence series, the maximum difference in interval may be associated with two series which are nearly coincident. The comparison of table 27 with table 28 shows that the effect of changing temperature on the average interval of a salt is almost negligible, but that the two components of one series of the $+20°$ spectrum may vary by as much as 1.9 units in frequency interval.

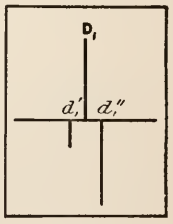

FIG. 63.

The character of the change in the absorption spectra when we pass from $+20°$ to $-185°$ can best be seen in detail by plotting a single group in the spectrum of each salt, as has been done for group 9 in figure 62. A better idea of the phenomena of cooling, as a whole, is obtained by means of maps like those in figures 64, 65, 66, and 67, in which all the bands of fluorescence and absorption are given at both temperatures, first in a single line as they occur in the spectrum of each salt. Fluorescence is indicated by vertical lines above the horizontal and absorption below. Length of line indicates roughly the strength

of the bands. No attempt has been made to denote the width of the bands. Below each spectrum the absorption bands are sorted out into their respective series. The figure is necessarily on a greatly reduced scale. Our working maps of these spectra are about 2 meters in width.

From these maps some of the statements already made can be verified at a glance; *e. g.*, the increased number of bands and series at −185°; the greater extent of absorption toward the red at +20° than at −185°, and that there is in general a greater degree of resolution of absorption than of fluorescence. It may also be noted that the known absorption spectrum is of greater extent than the fluorescence spectrum and that the absorption, considered as a unit, suffers a narrowing on cooling which is more marked on the side toward the red.

TABLE 28.—*Average intervals of absorption series at −185° C.*

Series.	K.	NH_4.	Rb.	Cs.	Average.	Series.	K.	NH_4.	Rb.	Cs.	Average.
b_1'	70.6			70.4	70.50	e_1'			70.7		70.70
b_1		71.4			71.40	e_1	70.6	70.7	70.9		70.73
b_1''			71.3		71.30	e_2'	70.5			70.0	70.25
b_2'		71.0		70.6	70.80	e_2			70.8	70.3	70.55
b_2	70.5		70.7	70.2	70.47	e_2''		71.4		70.8	71.10
b_2''		71.4			71.40						
b_3		71.2		70.7	70.95	*e* av.					70.67
b av.					70.83	a_1'			71.0	71.0	71.00
						a_1	70.0	71.3			70.65
c_1'				70.3	70.30	a_2	70.4		70.4	70.6	70.47
c_1			70.7	70.5	70.60	a_2''	71.9				71.90
c_2'	69.3			70.9	70.10						
c_2	70.0	70.9	70.4		70.43	*a* av.					71.00
c_2''	69.0		70.9		69.95						
c av.					70.28	Av.	70.22	71.06	70.84	70.54	
d_1	69.8		70.9		70.35						
d_1''		70.8		70.2	70.50						
d_2'			71.2	70.5	70.85						
d_2	70.0			71.0	70.50						
d_2''		70.5	71.1	70.7	70.68						
d_3	70.2				70.20						
d av.					70.51						

REVERSALS AND THE REVERSING REGION.

The phenomena of the reversing region, where fluorescence and absorption overlap, are complicated. Some points applicable particularly to the double chlorides are, however, discussed here.

The early observers of uranyl spectra were of the opinion that some connection or relation must exist between the system of bands of fluorescence and absorption. Becquerel and Onnes, who first studied these spectra at low temperatures, were able to confirm the impression of Stokes that the two systems overlapped and that there was actual

coincidence of position between certain fluorescence bands and absorption bands.

In the case of the double chlorides at +20°, each series of bands of the fluorescence system comes into coincidence, or near coincidence, with an absorption band in what we have termed the reversing region, which is approximately that region occupied by group 7 of the fluorescence spectrum.

The fact that the reversal sometimes appears to be exact, within the errors of observation, while sometimes there is a displacement of several units of frequency, might seem to render such a general relation doubtful, but the discrepancy can be shown to be a necessary consequence of the fact that both fluorescence and absorption bands at this temperature are unresolved complexes. The true nature of the case may be

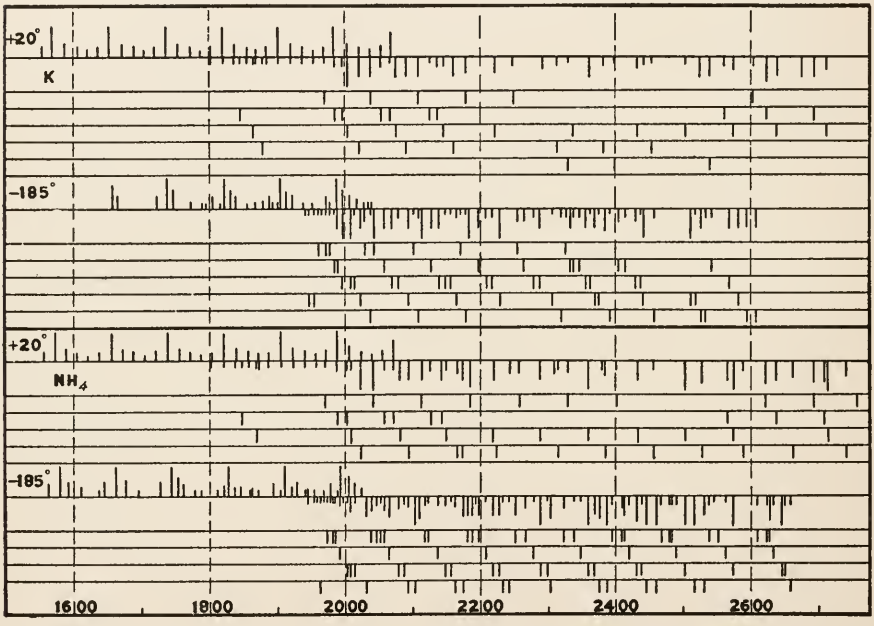

Fig. 64.

Fig. 65.

seen from figure 68, which is from a sketch of such a reversal at −185°, where the resolution is more nearly complete. Here the fluorescence and absorption are complementary, the strong components of fluorescence coinciding with the weak absorption component and vice versa. When the resolution is less complete, the weaker components will disappear, and although the reversal for each component is exact, there will be an apparent failure to reverse, or, in other words, we see the strong components displaced.

An actual instance in which this relation between fluorescence appears is given in plate 1, *a*, which is from a photograph of a small portion of the reversing region. The upper half contains the components of a resolved fluorescence band, the lower half the correspond-

ing components of the absorption band with fluorescence eliminated. In this photograph each component of the fluorescence has its exact reversal in absorption, with reciprocal relations as to intensity indicated in figure 68. The weaker component of fluorescence is coincident with the stronger component of the absorption doublet, and vice versa.

In the reversing region fluorescence and absorption are mutually destructive. Consequently one or both are sometimes invisible; but knowing the intervals, we can locate the reversal. By proper screening the fluorescence may be prevented and the absorption band brought out; and by taking extra precautions to secure a dark background and to increase the excitation the fluorescence may be seen. Thus the computation may be confirmed.

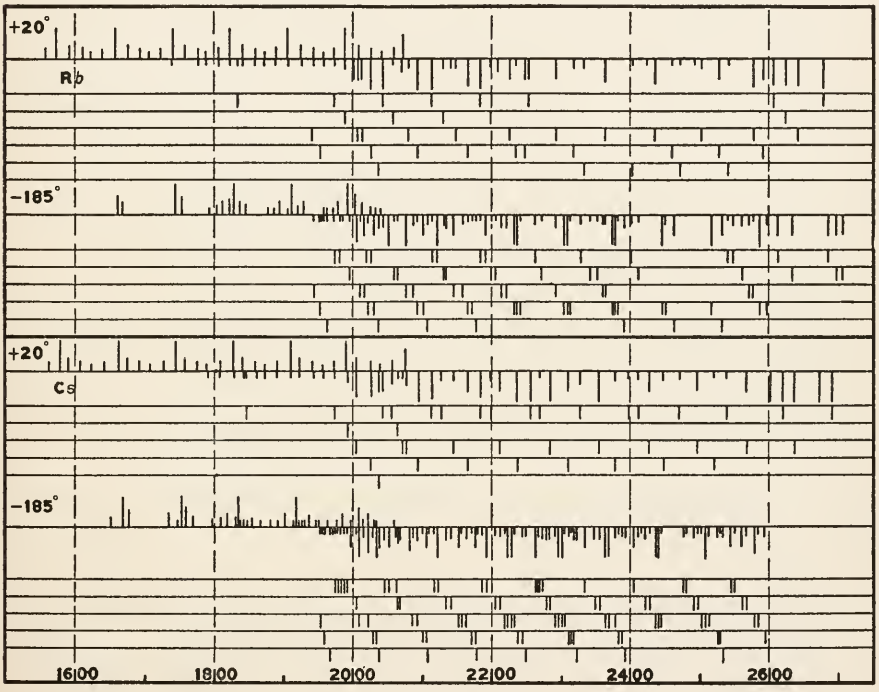

Fig. 66.

Fig. 67.

In the study of the double chlorides the matter is further confused because the difference between the fluorescence interval (83+) and that of the absorption interval (70+) is approximately equal to the distance between neighboring bands in the fluorescence groups. An absorption series which comes into coincidence with band C, group 7, will therefore nearly coincide with band B, group 8, etc. Furthermore, the degree of resolution in the absorption spectrum, as has already been mentioned, is often greater than in the fluorescence spectrum, and certain series are observable of which the corresponding fluorescence bands can not be identified.

So far as the spectra at +20° are concerned, we find that:

(1) All absorption bands toward the violet from the reversing region occur in series with constant-frequency intervals.

(2) For every fluorescence series there is a corresponding absorption series.

Whether the relation between absorption and fluorescence outlined above is significant can best be determined by the study of the spectra for −185°.

If, for example, the explanation of the numerous instances of inexact coincidence is valid, we should expect exact reversals of the components; also that the components of the resolved absorption spectra form series definitely related to the components of the fluorescence spectra in a manner consistent with the system indicated for the spectra at +20°. From a study of the exactness of the reversals in the resolved spectra at low temperatures it appears that 25 out of 38 fluorescence series are certainly reversed and that 36 fluorescence series join absorption series in the seventh group. The experimental error in this group does not exceed 1.5 units. The difference in position between fluorescence and absorption is sometimes greater than 1.5, but this may be ascribed to the dissymmetry in the form of the bands.

Fluorescence bands have their crest toward the violet, absorption bands toward the red. In the case of reversals, these regions tend to annul each other, leaving a remnant of fluorescence on the red side and a remnant of absorption on the violet. The result is that in regions where fluorescence and absorption exist together, fluorescence bands are apt to be given too great a wavelength, and vice versa. In the C_2 series of the rubidium chloride, for example, there is a displacement of 2.6 units between the *observed* positions of fluorescence and absorption.

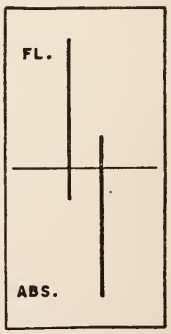

FIG. 68.

If, however, we compute the proper positions of these bands, using the average intervals for the C_2 and c_2 series respectively, thus eliminating the displacements in the reversal region, the fluorescence band and absorption thus established agree in position within 0.3 unit. The impossibility of excluding all absorption when fluorescence is present, and the impossibility of preventing a tendency toward fluorescence when absorption alone is sought for may well account for the resulting displacement. The case of the C_2 series is not an isolated one—probably every reversal is affected somewhat and the stronger bands the most; there being always an apparent shift of the absorption band toward the violet and of the fluorescence band toward the red. This phenomenon has long been recognized by the authors in connection with broad fluorescence bands, and it must now be recognized in the reversing of the narrow, line-like bands at the temperature of liquid air.

In the above, the reversals which connect fluorescence to absorption series have been sought for in the seventh group. There are, however, other possible connections, for coincidences occur in the sixth and eighth groups as well. Since, as has already been pointed out, the difference in spacing between a fluorescence and absorption interval is nearly the same as the spacing between fluorescence bands, it is often

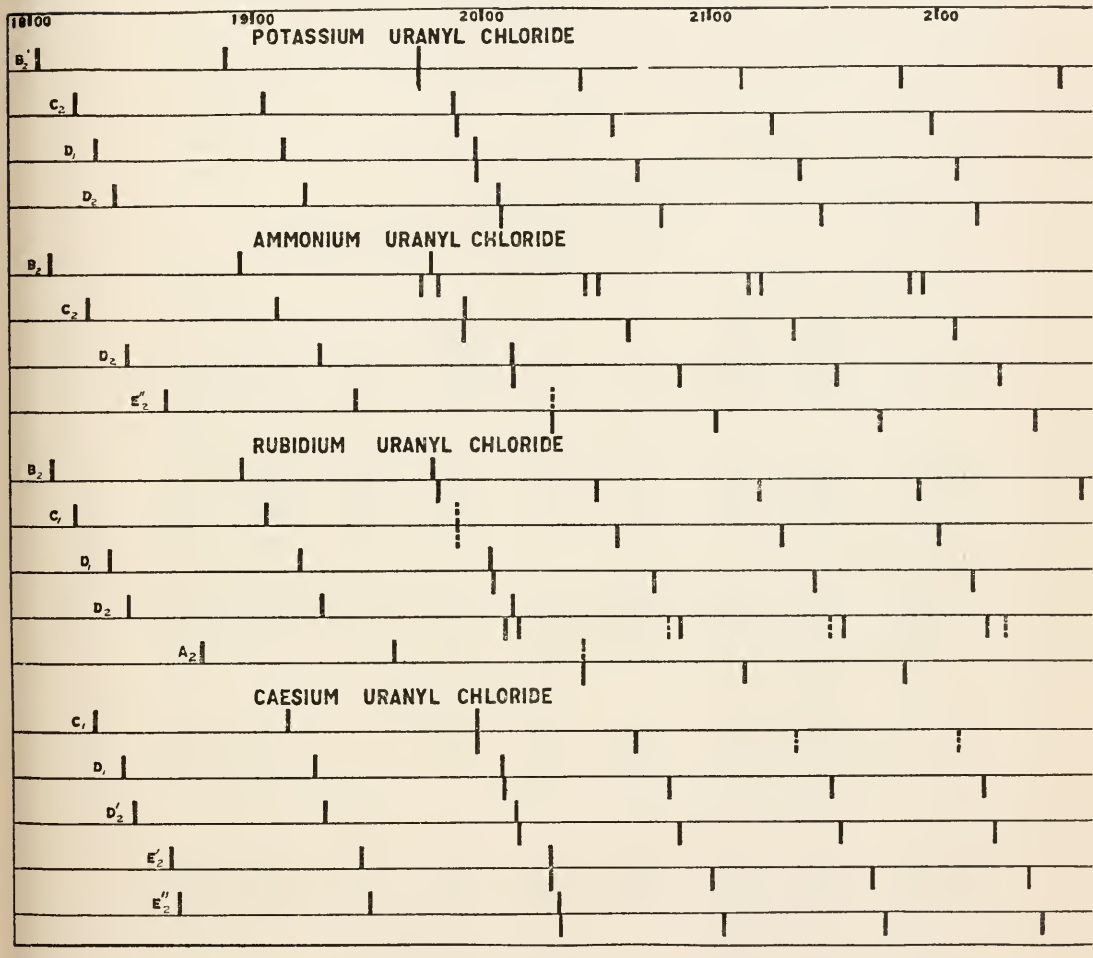

FIG. 69.

possible to join equally well two fluorescence series to one absorption series, a fact which makes it difficult to determine the true relation in the case of this class of salts.

The actual manner in which the reversals between fluorescence and absorption occur is shown in figure 69, which is a diagram of the reversing region. Here the plotting is quite accurate, the fluorescence bands above and the absorption bands below the horizontal. Dotted lines ndicate computed positions. This figure is approximately 10 times as

large as the original negatives. To avoid confusion, the various series occurring in each salt are vertically displaced instead of being drawn on a single line, as they appear in the actual spectra. An inspection of this diagram will suffice to indicate the approach to complete coincidence in the reversals and the type of departure from coincidence.

TABLE 29.—*General list of fluorescence bands in spectra of the double uranyl chlorides at +20° C.*

Group and series.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	λ	$\frac{1}{\lambda}\times10^3$	λ	$\frac{1}{\lambda}\times10^3$	λ	$\frac{1}{\lambda}\times10^3$	λ	$\frac{1}{\lambda}\times10^3$
1 B	.....	.....	0.6809	1469.7	.....	.....	.....	.....
1 C	.....	.....	.6716	1489.9	.....	.....	.....	.....
1 D	.....	.....	.6635	1507.1	.....	.....	.....	.....
1 E	.....	.....	.6571	1521.8	.....	.....	.....	.....
1 A	.....	.....	.6501	1538.2	.....	.....	.....	.....
2 B	0.6436	1553.7	.6430	1555.3	0.6420	1557.6	0.6401	1562.3
2 C	.6375	1568.6	.6358	1572.6	.6354	1573.8	.6336	1578.3
2 D	.6303	1586.6	.6291	1589.6	.6281	1592.2	.6289	1590.1
2 E	.6225	1606.4	.6231	1604.9	.6206	1611.3	.6219	1608.0
2 A	.6171	1620.5	.6172	1620.2	.6162	1622.8	.6156	1624.4
3 B	.6111	1636.5	.6103	1638.6	.6098	1640.0	.6090	1642.0
3 C	.6051	1652.5	.6041	1655.3	.6030	1658.3	.6015	1662.5
3 D	.5983	1671.5	.5978	1672.7	.5967	1675.9	.5970	1675.0
3 E	.5919	1689.5	.5923	1688.2	.5903	1694.1	.5911	1691.9
3 A	.5869	1704.0	.5866	1704.8	.5860	1706.4	.5854	1708.2
4 B	.5816	1719.4	.5813	1720.3	.5800	1724.0	.5789	1727.4
4 C	.5759	1736.4	.5752	1738.6	.5742	1741.6	.5729	1745.4
4 D	.5698	1754.9	.5696	1755.7	.5686	1758.7	.5689	1757.9
4 E	.5642	1772.3	.5642	1772.3	.5625	1777.8	.5631	1775.9
4 A	.5595	1787.2	.5593	1787.9	.5588	1789.4	.5587	1789.7
5 B	.5551	1801.4	.5546	1803.1	.5537	1806.1	.5529	1808.6
5 C	.5497	1819.3	.5492	1820.7	.5486	1822.8	.5472	1827.5
5 D	.5442	1837.6	.5436	1839.7	.5430	1841.5	.5433	1840.5
5 E	.5390	1855.3	.5385	1856.9	.5377	1859.8	.5379	1859.1
5 A	.5349	1869.6	.5342	1871.8	.5339	1873.1	.5339	1873.1
6 B	.5306	1884.7	.5300	1886.8	.5291	1890.0	.5288	1891.1
6 C	.5259	1901.5	.5250	1904.6	.5248	1905.5	.5234	1910.4
6 D	.5208	1920.1	.5200	1923.2	.5195	1925.0	.5198	1923.6
6 E	.5159	1938.3	.5153	1940.5	.5145	1943.5	.5147	1942.7
6 A	.5119	1953.5	.5112	1956.3	.5110	1957.1	.5113	1955.7
7 B	.5078	1969.4	.5072	1971.5	.5066	1973.8	.5067	1973.5
7 C	.5039	1984.4	.5031	1987.6	.5027	1989.1	.5024	1990.3
7 D	.4990	2004.0	.4986	2005.7	.4979	2008.4	.4989	2004.4
7 E	.4946	2021.7	.4940	2024.1	.4935	2026.2	.4937	2025.6
7 A	.4909	2036.9	.4904	2039.2	.4899	2041.4	.4904	2039.2
8 B	.4869	2053.8	.4867	2054.6	.4857	2059.0	.4863	2056.3
8 C	.4836	2068.0	.4829	2071.0	.4824	2072.8	.4819	2075.0
8 D	.....	.....	.....	.....	.....	.....	.....	.....
8 E	.....	.....	.....	.....	.....	.....	.....	.....
8 A	.....	.....	.....	.....	.....	.....	.....	.....

With regard to the reversing region at −185°, it can be stated that—

(1) The majority of the fluorescence series reverse in the seventh group.

(2) 36 out of 38 fluorescence series are joined in the seventh group to absorption series.

(3) The exactness of reversal depends not only on the structure of the band, but on the simultaneous presence of fluorescence and absorption in this region.

(4) Other reversals and connections are present in the groups adjacent to group 7.

TABLE 30.—*Frequencies and intervals of fluorescence series at +20° C.*

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.
K	Frequencies (observed)	.....	.....	1636.5	1719.4	1801.4	1884.7	1969.4	2053.8
	Frequencies (calculated)	.....	.....	1635.5	1718.9	1802.3	1885.7	1969.1	2052.6
	Differences	.....	.....	−1.0	−0.5	+0.9	+1.0	−0.3	−1.2
	Intervals (observed)	.....	.....		82.9	82.0	83.3	84.7	84.4
NH_4	Frequencies (observed)	1469.7	1555.3	1638.6	1720.3	1803.1	1886.8	1971.5	2054.6
	Frequencies (calculated)	1470.9	1554.3	1637.6	1720.9	1804.3	1887.6	1970.9	2054.3
	Differences	+1.2	−1.0	−1.0	+0.6	+1.2	+0.8	−0.6	−0.3
	Intervals (observed)		85.6	83.3	81.7	82.8	83.7	84.7	83.1
Rb	Frequencies (observed)	.....	1557.6	1640.0	1724.0	1806.1	1890.0	1973.8	2059.0
	Frequencies (calculated	.....	1556.2	1639.7	1723.2	1806.7	1890.1	1973.6	2057.1
	Differences	.....	−1.4	−0.3	−0.8	+0.6	+0.1	−0.2	−1.9
	Intervals (observed)	.....		83.4	84.0	82.1	83.9	83.8	85.2
Cs	Frequencies (observed)	.....	1562.3	1643.9	1727.4	1808.6	1891.1	1973.5	2056.3
	Frequencies (calculated)	.....	1562.0	1644.3	1726.6	1809.0	1891.3	1973.6	2055.9
	Differences	.....	−0.3	+0.4	−0.8	+0.4	+0.2	+0.1	−0.4
	Intervals (observed)	.....		81.6	83.5	81.2	82.5	82.4	82.8
				Series C.					
K	Frequencies (observed)	.....	1568.6	1652.5	1736.4	1819.3	1901.5	1984.4	2068.0
	Frequencies (calculated)	.....	1569.3	1652.4	1735.6	1818.7	1901.8	1984.9	2068.0
	Differences	.....	+0.7	−0.1	−0.8	−0.6	+0.3	+0.5	0.0
	Intervals	.....		83.9	83.9	82.9	82.2	82.9	83.6
NH_4	Frequencies (observed)	1489.9	1572.9	1655.3	1738.6	1820.7	1904.6	1987.6	2071.0
	Frequencies (calculated)	1489.4	1572.4	1655.4	1738.4	1821.4	1904.4	1987.4	2070.4
	Differences	−0.5	−0.5	+0.1	−0.2	+0.7	−0.2	−0.2	−0.6
	Intervals		83.0	82.4	83.3	82.1	83.9	83.0	83.4
Rb	Frequencies (observed)	.....	1573.8	1658.3	1741.6	1822.8	1905.5	1989.1	2072.8
	Frequencies (calculated)	.....	1574.5	1657.5	1740.4	1823.4	1906.4	1989.3	2072.3
	Differences	.....	+0.7	−0.8	−1.2	+0.6	+0.9	+0.2	−0.5
	Intervals	.....		84.5	83.3	81.2	82.7	83.6	83.7
Cs	Frequencies (observed)	.....	1578.5	1662.5	1745.4	1827.5	1910.4	1990.3	2075.0
	Frequencies (calculated)	.....	1579.6	1662.1	1744.6	1827.1	1909.6	1992.0	2074.6
	Differences	.....	+1.1	−0.4	−0.8	−0.4	−0.8	+1.7	−0.4
	Intervals	.....		84.0	82.9	82.1	82.9	79.9	84.7

TABLE 30.—*Frequencies and intervals of fluorescence series at +20° C*—continued.

Series D.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.
K	Frequencies (observed)	.....	1586.6	1671.5	1754.9	1837.6	1920.1	2004.0	.....
	Frequencies (calculated)	.....	1587.6	1670.9	1754.2	1837.5	1920.8	2004.1	.....
	Differences	.....	+1.0	−0.6	−0.7	−0.1	+0.7	+0.1	.....
	Intervals	.....		84.9	83.4	82.7	82.5	83.9	.....
NH_4	Frequencies (observed)	1507.1	1589.6	1672.7	1755.7	1839.7	1923.2	2005.7	.....
	Frequencies (calculated)	1506.6	1589.8	1673.0	1756.2	1839.4	1922.6	2005.8	.....
	Differences	−0.5	+0.2	+0.3	+0.5	−0.3	−0.6	+0.1	.....
	Intervals		82.5	83.1	83.0	84.0	83.5	82.5	.....
Rb	Frequencies (observed)	.....	1592.2	1675.9	1758.7	1841.5	1925.0	2008.4	.....
	Frequencies (calculated)	.....	1592.4	1675.6	1758.7	1841.9	1925.1	2008.2	.....
	Differences	.....	+0.2	−0.3	0.0	+0.4	+0.1	−0.2	.....
	Intervals	.....		83.7	82.8	82.8	83.5	83.4	.....
Cs	Frequencies (observed)	.....	1590.1	1675.0	1757.9	1840.5	1923.6	2004.4	.....
	Frequencies (calculated)	.....	1592.2	1675.0	1757.9	1840.7	1923.6	2006.4	.....
	Differences	.....	+1.1	0.0	0.0	+0.2	0.0	+2.0	.....
	Intervals	.....		84.9	82.9	82.6	83.1	80.8	.....

Series E.

K	Frequencies (observed)	.....	1606.4	1689.5	1772.3	1855.3	1938.3	2021.7	.....
	Frequencies (calculated)	.....	1606.4	1689.4	1772.4	1855.4	1938.4	2021.4	.....
	Differences	.....	0.0	−0.1	+0.1	+0.1	+0.1	−0.3	.....
	Intervals	.....		83.1	82.8	83.0	83.0	83.4	.....
NH_4	Frequencies (observed)	1521.8	1604.9	1688.2	1772.3	1856.9	1940.5	2024.1	.....
	Frequencies (calculated)	1521.2	1605.0	1688.8	1772.6	1856.4	1940.2	2024.0	.....
	Differences	−0.6	+0.1	+0.6	+0.3	−0.5	−0.3	−0.1	.....
	Intervals		83.1	83.3	84.1	84.6	83.6	83.6	.....
Rb	Frequencies (observed)	.....	1611.3	1694.1	1777.8	1859.8	1943.5	2026.2	.....
	Frequencies (calculated)	.....	1611.4	1694.1	1777.3	1860.3	1943.3	2026.2	.....
	Differences	.....	+0.1	0.0	−0.5	+0.5	−0.2	0.0	.....
	Intervals	.....		82.8	83.7	82.0	83.7	82.7	.....
Cs	Frequencies (observed)	.....	1608.0	1691.9	1775.9	1859.1	1942.7	2025.1	.....
	Frequencies (calculated)	.....	1608.4	1691.9	1775.4	1858.9	1942.3	2025.8	.....
	Differences	.....	+0.4	0.0	−0.5	−0.2	−0.4	+0.7	.....
	Intervals	.....		83.9	84.0	83.2	83.6	82.4	.....

Series A.

K	Frequencies (observed	.....	1620.5	1704.0	1787.2	1869.6	1953.5	2036.9	.....
	Frequencies (calculated)	.....	1620.5	1703.8	1787.0	1870.2	1953.5	2036.7	.....
	Differences	.....	0.0	−0.2	−0.2	+0.6	0.0	−0.2	.....
	Intervals	.....		83.5	83.2	82.4	83.9	83.4	.....
NH_4	Frequencies (observed)	1538.2	1620.2	1704.8	1787.9	1871.8	1956.3	2039.2	.....
	Frequencies (calculated)	1537.2	1620.9	1704.5	1788.2	1871.8	1955.5	2039.1	.....
	Differences	−1.0	+0.7	−0.3	+0.3	0.0	−0.8	−0.1	.....
	Intervals		82.0	84.6	83.1	83.9	84.5	82.9	.....
Rb	Frequencies (observed)	.....	.....	.....	1706.4	1789.4	1873.1	1957.1	2041.4	.....
	Frequencies (calculated)	.....	.....	.....	1706.0	1789.7	1873.5	1957.3	2041.0	.....
	Differences	.....	.....	.....	−0.4	+0.3	+0.4	+0.2	−0.4	.....
	Intervals	.....	.....	.....		83.0	83.7	84.0	84.3	.....
Cs	Frequencies (observed)	.....	1624.4	1708.2	1789.7	1873.1	1955.7	2039.2	.....
	Frequencies (calculated)	.....	1624.6	1707.4	1790.3	1873.1	1956.0	2038.8	.....
	Differences	.....	+0.2	+0.8	+0.6	0.0	+0.3	−0.4	.....
	Intervals	.....		83.8	81.5	83.4	82.6	83.5	.....

TABLE 31.—*General list of fluorescence bands in spectra of the double uranyl chlorides at −185° C.*

Group and series.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	λ	$\frac{1}{\lambda}\times 10^3$	λ	$\frac{1}{\lambda}\times 10^3$	λ	$\frac{1}{\lambda}\times 10^3$	λ	$\frac{1}{\lambda}\times 10^3$
2 B_2	.....	.....	0.6398	1563.0	.....	.....	.....	.....
2 C_2	.....	.....	.6330	1579.8	.....	.....	.....	.....
2 D_2	.....	.....	.6283	1591.5	.....	.....	.....	.....
2 E_2''	.....	.....	.6207	1611.0	.....	.....	.....	.....
3 B_1	.....	.....	.6110	1636.7	.....	.....	.....	.....
3 B_2	.....	.....	.6079	1645.0	.....	.....	0.6056	1651.3
3 C_2	0.6035	1657.0	.6016	1662.1	0.6018	1661.7	.5991	1669.2
3 D_1	.6006	1665.0	.....	.....	.5990	1669.4	.5964	1676.7
3 D_2	.....	.....	.5968	1675.6	.....	.....	.....	.....
3 E_2''	.....	.....	.5899	1695.0	.....	.....	.....	.....
4 B_2	.5803	1723.2	.5791	1726.9	.....	.....	.5764	1734.9
4 C_1	.....	.....	.....	.....	.....	.....	.5721	1747.9
4 C_2	.5752	1738.4	.5733	1744.4	.5731	1745.0	.5705	1752.7
4 D_1	.5724	1747.0	.5704	1753.1	.5703	1753.4	.5684	1759.4
4 D_2	.....	.....	.5677	1761.4	.....	.....	.5652	1769.3
4 E_2'	.5641	1772.7	.....	.....	.....	.....	.....	.....
4 E_2''	.....	.....	.5624	1778.1	.....	.....	.....	.....
4 A_1	.5603	1784.6	.5595	1787.3	.....	.....	.....	.....
4 A_2	.....	.....	.....	.....	.5573	1794.5	.5564	1797.2
5 B_1	.5569	1795.8	.....	.....	.5546	1803.1	.5526	1809.5
5 B_2	.5542	1804.4	.5524	1810.4	.5520	1811.5	.5500	1818.1
5 C_1	.5508	1815.5	.5493	1820.5	.5489	1821.9	.5464	1830.2
5 C_2	.5489	1821.7	.5471	1827.7	.5471	1827.8	.5452	1834.1
5 D_1'	.....	.....	.....	.....	.....	.....	.5440	1838.2
5 D_1	.5461	1831.0	.5445	1836.7	.5444	1836.9	.5427	1842.5
5 D_2'	.....	.....	.....	.....	.....	.....	.5412	1847.7
5 D_2	.5437	1839.4	.5420	1845.1	.5419	1845.2	.5395	1853.7
5 E_2'	.5389	1855.7	.5379	1859.0	.....	.....	.....	.....
5 E_2''	.....	.....	.5370	1862.0	.....	.....	.5358	1866.4
5 A_1	.5354	1867.6	.5345	1870.8	.....	.....	.....	.....
5 A_2	.....	.....	.....	.....	.5326	1877.7	.5318	1880.4
6 B_1	.5321	1879.5	.....	.....	.5300	1886.8	.5286	1891.8
6 B_2	.5297	1888.0	.5279	1894.4	.5277	1895.0	.5260	1901.1
6 B^3	.5279	1894.3	.....	.....	.....	.....	.....	.....
6 C_1	.5262	1900.4	.5250	1904.8	.5247	1905.9	.5223	1914.6
6 C_2	.5250	1904.6	.5234	1910.6	.5231	1911.7	.5214	1918.0
6 D_1'	.....	.....	.....	.....	.....	.....	.5201	1922.7
6 D_1	.5226	1913.5	.5206	1921.0	.5207	1920.3	.5191	1926.3
6 D_2'	.....	.....	.....	.....	.....	.....	.5179	1930.9
6 D_2	.5200	1922.9	.5184	1929.2	.5182	1929.9	.5163	1937.9
6 E_2'	.5155	1939.9	.5149	1941.9	.....	.....	.5137	1946.8
6 E_2''	.....	.....	.5141	1945.0	.....	.....	.5127	1950.4
6 A_1	.5124	1951.6	.5118	1953.7	.5107	1957.9	.....	.....
6 A_2	.....	.....	.....	.....	.5098	1961.6	.5092	1963.9
7 B_1	.5092	1963.9	.5080	1968.7	.5073	1971.4	.5059	1976.5
7 B_2	.5070	1972.3	.5056	1977.9	.5054	1978.6	.5038	1984.9
7 B_3	.5056	1977.8	.....	.....	.....	.....	.....	.....
7 C_1	.....	.....	.5028	1988.7	.....	.....	.5006	1997.6
7 C_2	.5031	1987.6	.5018	1992.7	.5018	1993.0	.....	.....
7 D_1	.5007	1997.2	.4989	2004.5	.4991	2003.7	.4979	2008.5
7 D_2'	.....	.....	.....	.....	.....	.....	.4963	2014.9
7 D_2	.4982	2007.4	.4967	2013.4	.4967	2013.2	.4950	2020.2
7 E_1	.4956	2017.8	.....	.....	.4938	2025.1	.....	.....
7 E_2'	.....	.....	.4940	2024.1	.....	.....	.4926	2030.0
7 E_2''	.....	.....	.....	.....	.....	.....	.4918	2033.3
7 A_1'	.4930	2028.4	.....	.....	.4917	2033.8	.....	.....
7 A_1	.4916	2034.2	.....	.....	.4902	2040.0	.....	.....
7 A_2	.4904	2039.2	.....	.....	.....	.....	.....	.....
8 B_1	.....	.....	.....	.....	.....	.....	.4857	2058.9

TABLE 32.—*Frequencies and intervals of fluorescence bands in the spectra of the four double chlorides at −185° C.*

Series and group	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.
B_1 3	.....	.....	1636.7	.....	.....	.....	.....	.....
5	1795.8	.....	.....	.....	1803.1	.....	1809.5	.....
	.....	83.7	.....	4×83.0	.....	83.7	.....	82.3
6	1879.5	.....	.....	.....	1886.8	.....	1891.8	.....
	.....	84.4	.....	.....	.....	84.6	.....	84.7
7	1963.9	.....	1968.7	.....	1971.4	.....	1976.5	.....
	.....	.....	.....	.....	.....	.....	.....	82.4
8	.....	.....	.....	.....	.....	.....	2058.9	.....
B_2 2	.....	.....	1563.0	.....	.....	.....	.....	.....
	.....	.....	.....	82.0	.....	.....	.....	.....
3	.....	.....	1645.0	.....	.....	.....	1651.3	.....
	.....	.....	.....	81.9	.....	.....	.....	83.6
4	1723.2	.....	1726.9	.....	.....	.....	1734.9	.....
	.....	81.2	.....	83.5	.....	.....	.....	83.2
5	1804.4	.....	1810.4	.....	1811.5	.....	1818.1	.....
	.....	83.6	.....	84.0	.....	83.5	.....	83.0
6	1888.0	.....	1894.4	.....	1895.0	.....	1901.1	.....
	.....	84.3	.....	83.5	.....	83.6	.....	83.8
7	1972.3	.....	1977.9	.....	1978.6	.....	1984.9	.....
B_3 6	1894.3	.....	.....	.....	.....	.....	.....	.....
	.....	83.5	.....	.....	.....	.....	.....	.....
7	1977.8	.....	.....	.....	.....	.....	.....	.....
C_1 4	.....	.....	.....	.....	.....	.....	1747.9	.....
	.....	.....	.....	.....	.....	.....	.....	82.3
5	1815.5	.....	1820.5	.....	1821.9	.....	1830.2	.....
	.....	84.9	.....	84.3	.....	84.0	.....	84.4
6	1900.4	.....	1904.8	.....	1905.9	.....	1914.6	.....
	.....	.....	83.9	.....	.....	.....	.....	83.0
7	.....	.....	1988.7	.....	.....	.....	1997.6	.....
C_2 2	.....	.....	1579.8	.....	.....	.....	.....	.....
	.....	.....	.....	82.3	.....	.....	.....	.....
3	1657.0	.....	1662.1	.....	1661.7	.....	1669.2	.....
	.....	81.4	.....	82.3	.....	83.3	.....	83.5
4	1738.4	.....	1744.4	.....	1745.0	.....	1752.7	.....
	.....	83.3	.....	82.3	.....	82.8	.....	81.4
5	1821.7	.....	1827.7	.....	1827.8	.....	1834.1	.....
	.....	82.9	.....	82.9	.....	83.9	.....	83.9
6	1904.6	.....	1910.6	.....	1911.7	.....	1918.0	.....
	.....	83.0	.....	82.1	.....	81.3	.....	.....
7	1987.6	.....	1992.7	.....	1993.0	.....	.....	.....
D_1' 5	.....	.....	.....	.....	.....	.....	1838.2	.....
	.....	.....	.....	.....	.....	.....	.....	84.5
6	.....	.....	.....	.....	.....	.....	1922.7	.....
D_1 3	1665.0	.....	.....	.....	1669.4	.....	1676.7	.....
	.....	82.0	.....	.....	.....	84.0	.....	82.7
4	1747.0	.....	1753.1	.....	1753.4	.....	1759.4	.....
	.....	84.0	.....	83.6	.....	83.5	.....	83.1
5	1831.0	.....	1836.7	.....	1836.9	.....	1842.5	.....
	.....	82.5	.....	84.3	.....	83.4	.....	83.8
6	1913.5	.....	1921.0	.....	1920.3	.....	1926.3	.....
	.....	83.7	.....	83.5	.....	83.4	.....	82.2
7	1997.2	.....	2004.5	.....	2003.7	.....	2008.5	.....

TABLE 32.—*Frequencies and intervals of fluorescence bands in the spectra of the four double chlorides at −185° C.*—continued.

Series. and group		Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
		$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.	$\frac{1}{\mu}\times10^3$	Interval.
D_2'	5	.....	.....	.....	.....	.....	.....	1847.7	.....
		.....	.....	.....	.....	.....	.....	.....	83.2
	6	.....	.....	.....	.....	.....	.....	1930.9	.....
		.....	.....	.....	.....	.....	.....	.....	84.0
	7	.....	.....	.....	.....	.....	.....	2014.9	.....
D_2	2	.....	.....	1591.5	.....	.....	.....	.....	.....
		.....	.....	.....	84.1	.....	.....	.....	.....
	3	.....	.....	1675.6	.....	.....	.....	.....	.....
		.....	.....	.....	85.8	.....	.....	.....	.....
	4	.....	.....	1761.4	.....	.....	.....	1769.3	.....
		.....	.....	.....	83.7	.....	.....	.....	84.4
	5	1839.4	.....	1845.1	.....	1845.2	.....	1853.7	.....
		.....	83.5	.....	84.1	.....	84.7	.....	83.3
	6	1922.9	.....	1929.2	.....	1929.9	.....	1937.0	.....
		.....	84.5	.....	84.2	.....	83.3	.....	83.2
	7	2007.4	.....	2013.4	.....	2013.4	.....	2020.2	.....
E_2'	4	1772.7	.....	.....	.....	.....	.....	.....	.....
		.....	83.0	.....	.....	.....	.....	.....	.....
	5	1855.7	.....	1859.0	.....	.....	.....	.....	.....
		.....	84.2	.....	82.9	.....	.....	.....	.....
	6	1939.9	.....	1941.9	.....	.....	.....	1946.8	.....
		.....	.....	.....	82.2	.....	.....	.....	83.2
	7	.....	.....	2024.1	.....	.....	.....	2030.0	.....
E_2''	2	.....	.....	1611.0	.....	.....	.....	.....	.....
		.....	.....	.....	84.0	.....	.....	.....	.....
	3	.....	.....	1695.0	.....	.....	.....	.....	.....
		.....	.....	.....	83.1	.....	.....	.....	.....
	4	.....	.....	1778.1	.....	.....	.....	.....	.....
		.....	.....	.....	83.9	.....	.....	.....	.....
	5	.....	.....	1862.0	.....	.....	.....	1866.4	.....
		.....	.....	.....	83.0	.....	.....	.....	84.0
	6	.....	.....	1945.0	.....	.....	.....	1950.4	.....
		.....	.....	.....	.....	.....	.....	.....	82.9
	7	.....	.....	.....	.....	.....	.....	2033.3	.....
A_1'	7	2028.4	.....	.....	.....	2033.8	.....	.....	.....
A_1	4	1784.6	.....	1787.3	.....	.....	.....	.....	.....
		.....	83.0	.....	83.5	.....	.....	.....	.....
	5	1867.6	.....	1870.8	.....	.....	.....	.....	.....
		.....	84.6	.....	82.9	.....	.....	.....	.....
	6	1951.6	.....	1953.7	.....	1957.9	.....	.....	.....
		.....	82.6	.....	.....	.....	82.1	.....	.....
	7	2034.2	.....	.....	.....	2040.0	.....	.....	.....
A_2	4	.....	.....	.....	.....	1794.5	.....	1797.2	.....
		.....	.....	.....	.....	.....	83.2	.....	83.2
	5	.....	.....	.....	.....	1877.7	.....	1880.4	.....
		.....	.....	.....	.....	.....	83.9	.....	83.5
	6	.....	.....	.....	.....	1961.6	.....	1963.9	.....
	7	2039.2	.....	.....	.....	.....	.....	.....	.....

TABLE 33.—*General list of absorption bands in spectra of the double uranyl chlorides at +20° C.*

Series b.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
1970.1	.....	1970.1	.....	1974.0	.....	1974.2	.....
.....	68.4	.....	71.1	.....	70.0	.....	69.1
2038.5	.....	2041.2	.....	2044.0	.....	2043.3*	.....
.....	70.3	.....	71.8	.....	70.4	.....	70.6
2108.8	.....	2113.0	.....	2114.4	.....	2113.9	.....
.....	70.8	.....	72.0	.....	70.2	.....	70.4
2179.6	.....	2185.0	.....	2184.6	.....	2184.3	.....
.....	68.2	.....	71.2	.....	69.5	.....	71.0
2247.8	}	2256.2	.....	2253.1	}	2255.3	.....
———		.....	73.3	———		.....	71.7
———		2329.5	.....	———		2327.0*	.....
———		.....	70.8	———		.....	71.4
———		2400.3	}	———		2398.4	.....
———	71.0×5	———		———	70.7×5	.....	72.6
———		———		———		2471.0	.....
———		———		———		.....	68.7
———		———	71.3×5	———		2539.7	.....
2603.0	}	———		2606.5	}	.....	.....
.....	72.0	———		.....	73.0	.....	.....
2675.0	.....	———		2679.5	.....	.....	.....
.....	.....	2756.8	}	.....	.....	.....	.....

Series b″.

.....	.....	2620.9	.....	.....	.....	.....	.....
.....	.....	.....	71.9	.....	.....	.....	.....
.....	.....	2692.8	.....	.....	.....	.....	.....

Series β.

.....	.....	.....	.....	.....	.....	2056.0	.....
.....	.....	.....	.....	.....	.....	.....	71.1
.....	.....	.....	.....	.....	.....	2127.1	.....
.....	.....	.....	.....	.....	.....	.....	72.2
.....	.....	.....	.....	.....	.....	2199.3	.....
.....	.....	.....	.....	.....	.....	.....	70.3
.....	.....	.....	.....	.....	.....	2269.6	}
.....	.....	.....	.....	.....	.....	———	70.9×2
.....	.....	.....	.....	.....	.....	2411.4	}
.....	.....	.....	.....	.....	.....	.....	
.....	.....	.....	.....	.....	.....	———	69.7×3
.....	.....	.....	.....	.....	.....	2620.5	}
.....	.....	.....	.....	.....	.....	.....	71.3
.....	.....	.....	.....	.....	.....	2691.8	.....

* These bands were doubled occasionally.

TABLE 33.—*General list of absorption bands in spectra of the double uranyl chlorides at +20° C.*—continued.

Series c.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
1985.2	.....	1988.5	.....	1989.1	.....	1993.1	.....
.....	68.6	.....	69.0	.....	68.5	.....	71.3
2053.8	.....	2057.5	.....	2057.6	.....	2064.4	.....
.....	71.6	.....	68.5	.....	72.8	.....	.....
2125.4		2126.0	.....	2130.4	.....	.....	.....
———		.....	.....	.....	68.9	.....	.....
———		.....	.....	2199.3		.....	.....
———		.....	.....	———		.....	.....
———	71.2×7	.....	.....	———	70.8×6	.....	.....
———		.....	.....	———		.....	.....
———		.....	.....	———		.....	.....
———		.....	.....	———		.....	.....
2623.8		.....	.....	2624.5		.....	.....
.....	69.5	.....	.....	.....	.....	.....	.....
2693.3	.....	.....	.....	.....	.....	.....	.....

Series γ.

1997.0	.....	2001.6	.....	2001.0	.....	.....	.....
.....	70.4	.....	69.0	.....	69.5	.....	.....
2067.4	.....	2070.6	.....	2070.5	.....	.....	.....
.....	70.6	.....	72.0	.....	70.8	.....	.....
2137.0		2142.6		2141.3	.....	.....	.....
———		———		.....	67.7	.....	.....
———		———		2209.0		.....	.....
———		———		———		.....	.....
———	70.5×6	———	70.4×6	———	71.6×3	.....	.....
———		———		2423.7		.....	.....
———		———		.....	69.4	.....	.....
———		———		2493.1	.....	.....	.....
2560.2		2565.1		.....	.....	.....	.....
.....	.....	.....	72.0	.....	.....	.....	.....
.....	.....	2637.1	.....	.....	.....	.....	.....
.....	.....	.....	71.5	.....	.....	.....	.....
.....	.....	2708.6	.....	.....	.....	.....	.....

Series d'.

.....	.....	.....	.....	.....	.....	2071.3	
.....	.....	.....	.....	.....	.....	———	70.4×2
.....	.....	.....	.....	.....	.....	2212.2	
.....	.....	.....	.....	.....	.....	.....	72.8
.....	.....	.....	.....	.....	.....	2284.0	.....
.....	.....	.....	.....	.....	.....	.....	70.6
.....	.....	.....	.....	.....	.....	2354.6	.....
.....	.....	.....	.....	.....	.....	.....	72.0
.....	.....	.....	.....	.....	.....	2426.6	.....
.....	.....	.....	.....	.....	.....	.....	70.0
.....	.....	.....	.....	.....	.....	2496.6	.....
.....	.....	.....	.....	.....	.....	.....	72.1
.....	.....	.....	.....	.....	.....	2568.7	.....
.....	.....	.....	.....	.....	.....	.....	68.1
2638.9	.....	.....	.....	2642.0	.....	2636.8	.....
.....	73.3	.....	.....	.....	.....	.....	.....
2712.2	.....	2713.7	.....	.....	.....	.....	.....

TABLE 33.—*General list of absorption bands in spectra of the double uranyl chlorides at +20° C.*—continued.

Series d.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2004.3	.....	.....	.....	2007.1	.....	2004.9	.....
.....	70.8	.....	.....	.....	73.0	.....	71.4
2075.1	.....	.....	.....	2080.1	.....	2076.3	.....
.....	71.3	.....	.....	.....	69.1	.....	69.2
2146.4	.....	.....	.....	2149.2	}	2145.5	.....
.....	.....	2218.9	.....	———	}71.9×2	.....	.....
.....	.....	.....	69.6	———	}	.....	.....
.....	.....	2288.5	.....	2293.1	}	.....	.....
.....	.....	.....	71.4	.....	71.7	.....	.....
.....	.....	2359.9	.....	2364.8	.....	.....	.....
.....	.....	.....	72.1	.....	70.6	.....	.....
.....	.....	2432.0	.....	2435.4	.....	.....	.....
.....	.....	.....	69.8	.....	68.5	.....	.....
.....	.....	2501.8	.....	2503.9	.....	.....	.....
.....	.....	.....	71.9	.....	73.8	.....	.....
.....	.....	2573.7	.....	2577.7	.....	.....	.....

Series d''.

.....	.....	2008.9	.....	2013.7	}	.....	.....
.....	.....	.....	71.2	.....	}	.....	.....
.....	.....	2080.1	.....	.....	}70.8×3	.....	.....
.....	.....	.....	69.4	———	}	.....	.....
.....	.....	2149.5	.....	———	}	.....	.....
2221.8	.....	.....	.....	2226.0	}	.....	.....
.....	70.1	.....	.....	.....	.....	.....	.....
2291.9	.....	.....	.....	.....	.....	.....	.....
.....	69.4	.....	.....	.....	.....	.....	.....
2361.3	.....	.....	.....	.....	.....	.....	.....
.....	70.2	.....	.....	.....	.....	.....	.....
2431.5	.....	.....	.....	.....	.....	.....	.....
.....	71.6	.....	.....	.....	.....	.....	.....
2503.1	.....	.....	.....	.....	.....	.....	.....
.....	71.7	.....	.....	.....	.....	.....	.....
2574.8	.....	.....	.....	.....	.....	.....	.....

Series e.

2021.4	.....	2023.3	.....	2025.3	.....	2025.6	.....
.....	69.5	.....	70.7	.....	69.6	.....	69.1
2090.9	.....	2094.0	.....	2094.9	.....	2094.7	.....
.....	70.1	.....	71.5	.....	71.5	.....	70.9
2161.0	}	2165.5	}	2166.4	.....	2165.6	.....
.....	}	.....	}	.....	69.2	.....	72.4
.....	}	———	}71.7×2	2235.6	}	2237.0	.....
.....	}	———	}	.....	}	.....	73.0
.....	}70.2×4	2309.0	}	.....	}	2310.0	.....
———	}	.....	70.9	.....	}	.....	68.2
———	}	2379.9	}	.....	}71.3×5	2378.2	.....
———	}	.....	}	———	}	.....	69.8
2442.0	}	.....	}69.6×3	———	}	2448.0	.....
.....	}	———	}	———	}	.....	72.2
.....	}	———	}	———	}	2520.2	.....
.....	.....	2588.7	}	2592.0	}	.....	.....
.....	.....	.....	73.0	.....	.....	.....	.....
.....	.....	2661.7	.....	.....	.....	.....	.....

TABLE 33.—*General list of absorption bands in spectra of the double uranyl chlorides at +20° C.*—continued.

Series e''.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
.....	.....	2173.5	.....	.....	.....	.....	.....
.....	.....	.....	71.0	.....	.....	.....	.....
.....	.....	2244.5	.....	2248.5	.....	.....	.....
.....	.....	.....	70.1	.....	69.5	.....	.....
2313.0	.....	2314.6	.....	2318.0	.....	.....	.....
.....	68.6	.....	70.0	.....	67.7	.....	.....
2381.6	.....	2384.6	.....	.....	}	.....	.....
.....	71.2	.....	70.6	———	}71.0×2	.....	.....
2452.8	.....	2455.2	.....	2460.0	}	.....	.....
.....	71.2	.....	72.2	.....	67.8	.....	.....
2524.0	.....	2527.4	}	2527.8	.....	.....	.....
.....	.....	———	}71.3×3	.....	.....	.....	.....
.....	.....	———	}	.....	.....	.....	.....
.....	.....	2741.2	}	.....	.....	.....	.....

Series a.

.....	.....	.....	.....	.....	.....	2037.1	}
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	———	}70.6×8
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	2602.2	.....
.....	.....	.....	.....	.....	.....	.....	72.0
.....	.....	.....	.....	.....	.....	2674.2	.....

Series a''.

2329.4	.....	.....	.....	2333.7	.....	.....	.....
.....	69.3	.....	.....	.....	70.2	.....	.....
2398.7	}	.....	.....	2403.9	.....	.....	.....
.....	}	.....	.....	.....	67.7	.....	.....
.....	}70.3×2	.....	.....	2471.6	.....	.....	.....
———	}	.....	.....	.....	70.5	.....	.....
2539.4	}	.....	.....	2542.1	.....	.....	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*

Series b_1'.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2029.1	.....	.....	.....	.....	.....	2045.3	.....
.....	71.7	.....	.....	.....	.....	.....	71.1
2100.8	.....	.....	.....	.....	.....	2116.4	.....
.....	70.1	.....	.....	.....	.....	.....	70.1
2170.9	.....	.....	.....	.....	.....	2186.5	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series b_1.

Potassium urany chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
.....	.....	2038.5	.....	.....	.....	.....	.....
.....	.....	.....	71.5	.....	.....	.....	.....
.....	.....	2109.0	.....	.....	.....	.....	.....
.....	.....	.....	71.2	.....	.....	.....	.....
.....	.....	2180.2	.....	.....	.....	.....	.....
.....	.....	.....	70.7	.....	.....	.....	.....
.....	.....	2250.9	.....	.....	.....	.....	.....
.....	.....	.....	71.9	.....	.....	.....	.....
.....	.....	2322.8	.....	.....	.....	.....	.....
.....	.....	.....	71.2	.....	.....	.....	.....
.....	.....	2394.0	.....	.....	.....	.....	.....
.....	.....	.....	72.8	.....	.....	.....	.....
.....	.....	2466.8	.....	.....	.....	.....	.....
.....	.....	.....	70.5	.....	.....	.....	.....
.....	.....	2537.3	.....	.....	.....	.....	.....
.....	.....	.....	72.7	.....	.....	.....	.....
.....	.....	2609.0	.....	.....	.....	.....	.....

Series b_1''.

.....	.....	.....	.....	2044.2	.....	.....	.....
.....	.....	.....	.....	.....	70.7	.....	.....
.....	.....	.....	.....	2114.9	.....	.....	.....
.....	.....	.....	.....	.....	70.0	.....	.....
.....	.....	.....	.....	2184.9	}	.....	.....
.....	.....	.....	.....	———	72.0×2	.....	.....
.....	.....	.....	.....	2328.8	}	.....	.....
.....	.....	.....	.....	.....	72.5	.....	.....
.....	.....	.....	.....	2401.3	}	.....	.....
.....	.....	.....	.....	———	69.9×2	.....	.....
.....	.....	.....	.....	2541.0	}	.....	.....
.....	.....	.....	.....	.....	72.4	.....	.....
.....	.....	.....	.....	2613.4	.....	.....	.....
.....	.....	.....	.....	.....	73.0	.....	.....
.....	.....	.....	.....	2686.4	.....	.....	.....

Series b_2'.

.....	.....	2045.5	.....	.....	.....	2051.6	.....
.....	.....	.....	71.4	.....	.....	.....	71.3
.....	.....	2116.9	.....	.....	.....	2122.9	.....
.....	.....	.....	70.8	.....	.....	.....	70.6
.....	.....	2187.7	.....	.....	.....	2193.5	.....
.....	.....	.....	.....	.....	.....	.....	69.5
.....	.....	.....	.....	.....	.....	2263.0	.....
.....	.....	.....	.....	.....	.....	.....	71.0
.....	.....	.....	.....	.....	.....	2334.0	.....
.....	.....	.....	.....	.....	.....	.....	70.7
.....	.....	.....	.....	.....	.....	2404.7	.....
.....	.....	.....	.....	.....	.....	.....	71.6
.....	.....	.....	.....	.....	.....	2476.3	.....
.....	.....	.....	.....	.....	.....	.....	69.2
.....	.....	.....	.....	.....	.....	2545.5	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series b_2.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2043.6	.....	.....	.....	2050.4	.....	.....	.....
.....	70.1	.....	.....	.....	71.0	.....	.....
2113.7	.....	.....	.....	2121.4	.....	.....	.....
.....	70.3	.....	.....	.....	70.2	.....	.....
2184.0	.....	.....	.....	2191.6	.....	.....	.....
.....	70.3	.....	.....	.....	71.1	.....	.....
2254.3	.....	.....	.....	2262.7	.....	2268.6	}
.....	71.3	.....	.....	.....	.....	———	}71.0×2
2325.6	.....	.....	.....	.....	.....	———	}
.....	.....	.....	.....	.....	.....	2410.5	
.....	.....	.....	.....	.....	.....	.....	70.1
.....	.....	.....	.....	.....	.....	2480.6	.....
.....	.....	.....	.....	.....	.....	.....	69.8
.....	.....	.....	.....	.....	.....	2550.4	.....

Series b_2''.

.....	.....	2051.1	.....	.....	.....	.....	.....
.....	.....	.....	71.6	.....	.....	.....	.....
.....	.....	2122.7	.....	.....	.....	.....	.....
.....	.....	.....	70.4	.....	.....	.....	.....
.....	.....	2193.1	.....	.....	.....	.....	.....
.....	.....	.....	72.8	.....	.....	.....	.....
.....	.....	2265.9	.....	.....	.....	.....	.....
.....	.....	.....	72.3	.....	.....	.....	.....
.....	.....	2338.2	.....	.....	.....	.....	.....
.....	.....	.....	70.5	.....	.....	.....	.....
.....	.....	2408.7	.....	.....	.....	.....	.....
.....	.....	.....	70.3	.....	.....	.....	.....
.....	.....	2479.0	.....	.....	.....	.....	.....
.....	.....	.....	71.1	.....	.....	.....	.....
.....	.....	2550.1	.....	.....	.....	.....	.....
.....	.....	.....	72.6	.....	.....	.....	.....
.....	.....	2622.7	.....	.....	.....	.....	.....

Series b_3.

.....	.....	2056.5	}	.....	.....	2061.9	}
.....	.....	———	}70.4×2	.....	.....	———	}70.6×3
.....	.....	2197.3	}	.....	.....	———	}
.....	.....	———	}	.....	.....	2273.8	}
.....	.....	———	}71.5×3	.....	.....	———	}70.9×2
.....	.....	2411.9	}	.....	.....	2415.5	}
.....	.....	.....	70.6	.....	.....	.....	.....
.....	.....	2482.5	}	.....	.....	.....	.....
.....	.....	———	}71.9×2	.....	.....	.....	.....
.....	.....	2626.3	}	.....	.....	.....	.....

Series C_1'.

.....	.....	.....	.....	.....	.....	2064.3	.....
.....	.....	.....	.....	.....	.....	.....	70.6
.....	.....	.....	.....	.....	.....	2134.9	.....
.....	.....	.....	.....	.....	.....	.....	70.0
.....	.....	.....	.....	.....	.....	2204.9	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series C_1.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
.....	.....	.....	.....	2059.—	.....	2067.8	70.3×3
.....	.....	.....	.....	.....	72.0	———	
.....	.....	.....	.....	2131.3	.....	———	
.....	.....	.....	.....	.....	68.7	.....	
.....	.....	.....	.....	2200.0	.....	.....	
.....	.....	.....	.....	.....	72.0	.....	.....
.....	.....	.....	.....	2272.0	.....	2278.7	.....
.....	.....	.....	.....	.....	69.9	.....	71.0
.....	.....	.....	.....	2341.9	.....	2349.7	.....
.....	.....	.....	.....	.....	69.5	.....	71.6
.....	.....	.....	.....	2411.4		2421.3	.....
.....	.....	.....	.....	———		.....	70.3
.....	.....	.....	.....	———		2491.6	.....
.....	.....	.....	.....	———	71.6×4	.....	68.9
.....	.....	.....	.....	.....		2560.5	.....
.....	.....	.....	.....	.....		.....	.....
.....	.....	.....	.....	2997.6		.....	.....

Series C_2'.

.....	.....	.....	.....	.....	.....	2141.3	.....
.....	.....	.....	.....	.....	.....	.....	71.1
.....	.....	.....	.....	.....	.....	2212.4	.....
.....	.....	.....	.....	.....	.....	.....	70.7
2264.2	.....	.....	.....	.....	.....	2283.1	.....
.....	68.5	.....	.....	.....	.....	.....	.....
2332.7	.....	.....	.....	.....	.....	.....	.....
.....	71.3	.....	.....	.....	.....	.....	.....
2404.0		.....	.....	.....	.....	.....	.....
———	69.2×2	.....	.....	.....	.....	.....	.....
2542.3		.....	.....	.....	.....	.....	.....

Series C_2.

2057.6	.....	2064.7	.....	2064.7	.....	.....	.....
.....	69.8	.....	71.8	.....	69.8	.....	.....
2127.4	.....	2136.5	.....	2134.5	.....	.....	.....
.....	69.9	.....	70.8	.....	70.9	.....	.....
2197.3		2207.3	.....	2205.4	.....	.....	.....
———		.....	71.0	.....	.....	.....	.....
———	70.3×2	2278.3	.....	.....	.....	.....	.....
.....		.....	69.8	.....	.....	.....	.....
2337.8		2348.1	.....	.....	.....	2356.0	.....
.....	.....	.....	70.9	.....	.....	.....	71.8
.....	.....	2419.0	.....	.....	.....	2427.8	.....
.....	.....	.....	70.9	.....	.....	.....	70.3
.....	.....	2489.9	.....	.....	.....	2498.1	.....
.....	.....	.....	71.7	.....	.....	.....	69.3
.....	.....	2561.6	.....	.....	.....	2567.4	.....
.....	.....	.....	71.4	.....	.....	.....	.....
.....	.....	2633.0	.....	.....	.....	.....	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series C_2''.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2346.1	.....	.....	.....	2352.4		.....	.....
.....	68.8	.....	.....	———		.....	.....
2414.9		.....	.....	———	69.7×3	.....	.....
———	69.1×2	.....	.....	.....		.....	.....
2553.0		.....	.....	2561.5		.....	.....
.....	.....	.....	.....	.....	72.9	.....	.....
.....	.....	.....	.....	2634.4	.....	.....	.....
.....	.....	.....	.....	.....	72.0	.....	.....
.....	.....	.....	.....	2706.4	.....	.....	.....

Series d_1.

2068.8	.....	.....	.....	2075.4	.....	.....	.....
.....	70.7	.....	.....	.....	70.3	.....	.....
2139.5	.....	.....	.....	2145.7	.....	.....	.....
.....	69.0	.....	.....	.....	69.2	.....	.....
2208.5	.....	.....	.....	2214.9		.....	.....
.....	70.0	.....	.....	.....	72.7×2	.....	.....
2278.5	.....	.....	.....	———		.....	.....
.....	.....	.....	.....	2360.2		.....	.....
.....	.....	.....	.....	———		.....	.....
.....	.....	.....	.....	———	70.4×3	.....	.....
.....	.....	.....	.....	2571.4		.....	.....

Series d_1''.

.....	.....	2006.8	.....	.....	.....	2009.6	.....
.....	.....	.....	71.1	.....	.....	.....	72.0
.....	.....	2077.9	.....	.....	.....	2081.6	.....
.....	.....	.....	71.0	.....	.....	.....	70.8
.....	.....	2148.9	.....	.....	.....	2152.4	.....
.....	.....	.....	69.3	.....	.....	.....	66.7
.....	.....	2218.2	.....	.....	.....	2219.1	.....
.....	.....	.....	70.3	.....	.....	.....	72.2
.....	.....	2288.5	.....	.....	.....	2291.3	
.....	.....	.....	70.6	.....	.....	.....	
.....	.....	2359.1	.....	.....	.....	———	70.5×2
.....	.....	.....	71.8	.....	.....	———	
.....	.....	2430.9	.....	.....	.....	2432.3	
.....	.....	.....	71.1	.....	.....	.....	69.6
.....	.....	2502.0	.....	.....	.....	2501.9	.....
.....	.....	.....	71.2	.....	.....	.....	.....
.....	.....	2573.2	.....	.....	.....	.....	.....
.....	.....	.....	72.3	.....	.....	.....	.....
.....	.....	2645.5	.....	.....	.....	.....	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series d_2'.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
.....	.....	.....	.....	2221.4	.....	2086.2	.....
.....	.....	.....	.....	.....	71.2	.....	70.2
.....	.....	.....	.....	2292.6	.....	2156.4	.....
.....	.....	.....	.....	.....	70.7	.....	67.3
.....	.....	.....	.....	2363.3	}	2223.7	.....
.....	.....	.....	.....	.....		.....	72.5
.....	.....	.....	.....	.....		2296.2	.....
.....	.....	.....	.....	———	71.3×3	.....	68.2
.....	.....	.....	.....	———		2364.4	.....
.....	.....	.....	.....	———		.....	72.0
.....	.....	.....	.....	2577.3	}	2436.4	.....
.....	.....	.....	.....	.....	.....	.....	72.1
.....	.....	.....	.....	.....	.....	2508.5	.....
.....	.....	.....	.....	.....	.....	.....	70.8
.....	.....	.....	.....	.....	.....	2579.3	.....

Series d_2.

2079.0	.....	.....	.....	.....	.....	.....	.....
.....	69.9	.....	.....	.....	.....	.....	.....
2148.9	.....	.....	.....	.....	.....	.....	.....
.....	68.2	.....	.....	.....	.....	.....	.....
2217.1	.....	.....	.....	.....	.....	2229.2	.....
.....	70.5	.....	.....	.....	.....	.....	71.6
2287.6	.....	.....	.....	.....	.....	2300.8	.....
.....	68.5	.....	.....	.....	.....	.....	68.6
2356.1	.....	.....	.....	.....	.....	2369.4	.....
.....	73.1	.....	.....	.....	.....	.....	71.4
2429.2	}	.....	.....	.....	.....	2440.8	.....
.....		.....	.....	.....	.....	.....	72.4
———	69.8×2	.....	.....	.....	.....	2513.2	.....
———		.....	.....	.....	.....	.....	71.4
2568.7	}	.....	.....	.....	.....	2584.6	.....

Series d_2''.

.....	.....	.....	.....	2016.1	.....	.....	.....
.....	.....	.....	.....	.....	70.1	.....	.....
.....	.....	2086.8	.....	2086.2	.....	2092.7	.....
.....	.....	.....	68.7	.....	72.0	.....	71.1
.....	.....	2155.5	.....	2158.2	.....	2163.8	.....
.....	.....	.....	71.5	.....	.....	.....	69.3
.....	.....	2227.0	.....	.....	.....	2233.1	.....
.....	.....	.....	71.0	.....	.....	.....	71.8
.....	.....	2298.0	.....	.....	.....	2304.9	.....
.....	.....	.....	70.3	.....	.....	.....	73.1
.....	.....	2368.3	.....	.....	.....	2378.0	.....
.....	.....	.....	69.6	.....	.....	.....	66.7
.....	.....	2437.9	}	.....	.....	2444.7	.....
.....	.....	———	70.7×3	.....	.....	.....	.....
.....	.....	———		.....	.....	.....	.....
.....	.....	2650.0	}	.....	.....	.....	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series d_3.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2014.0	70.6×2	.....	.....	.....	.....	.....	.....
2155.2		.....	.....	.....	.....	.....	.....
	69.2×3	.....	.....	.....	.....	.....	.....
2362.7		.....	.....	.....	.....	.....	.....
.....	73.6	.....	.....	.....	.....	.....	.....
2436.3	.....	.....	.....	.....	.....	.....	.....

Series e_1'.

.....	.....	.....	.....	2021.6	.....	.....	.....
.....	.....	.....	.....	.....	72.0	.....	.....
.....	.....	.....	.....	2093.6	69.8×2	.....	.....
.....	.....	.....	.....	2233.1		.....	.....
.....	.....	.....	.....	.....	71.1	.....	.....
.....	.....	.....	.....	2304.2	.....	.....	.....
.....	.....	.....	.....	.....	70.5	.....	.....
.....	.....	.....	.....	2374.7	.....	.....	.....
.....	.....	.....	.....	.....	71.5	.....	.....
.....	.....	.....	.....	2446.2	.....	.....	.....
.....	.....	.....	.....	.....	71.1	.....	.....
.....	.....	.....	.....	2517.3	.....	.....	.....
.....	.....	.....	.....	.....	70.2	.....	.....
.....	.....	.....	.....	2587.5	.....	.....	.....

Series e_1.

.....	.....	2092.7	.....	.....	.....	.....	.....
.....	.....	.....	69.4	.....	.....	.....	.....
.....	.....	2162.1	.....	2166.8	.....	.....	.....
.....	.....	.....	70.9	.....	69.9	.....	.....
2229.4		2233.0	.....	2236.7	.....	.....	.....
.....		.....	70.4	.....	72.3	.....	.....
———	69.9×2	2303.4	.....	2309.0	.....	.....	.....
———		.....	72.6	.....	68.7	.....	.....
2369.1		2376.0	.....	2378.7	.....	.....	.....
.....	71.9	.....	69.0	.....	71.9	.....	.....
2441.0	.....	2445.0	.....	2450.4	.....	.....	.....
.....	69.6	.....	70.8	.....	.....	.....	.....
2510.6	.....	2515.8		.....	.....	.....	.....
.....	71.4	.....	70.9×2	.....	.....	.....	.....
2582.0	.....	———		.....	.....	.....	.....
.....	.....	2657.5		.....	.....	.....	.....

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series e_2'.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
2023.4	.....	.....	.....	.....	.....	2029.6	.....
.....	71.1	.....	.....	.....	.....	.....	70.8
2094.5	.....	.....	.....	.....	.....	2100.4	.....
.....	70.5	.....	.....	.....	.....	.....	70.2
2165.0	}	.....	.....	.....	.....	2170.6	.....
———		.....	.....	.....	.....	.....	68.0
———	}70.3×2	.....	.....	.....	.....	2238.6	.....
———		.....	.....	.....	.....	.....	71.7
2305.5	}	.....	.....	.....	.....	2310.3	.....
.....	69.4	.....	.....	.....	.....	.....	.....
2374.9	}	.....	.....	.....	.....	.....	.....
———	}71.7×2	.....	.....	.....	.....	.....	.....
2518.3	}	.....	.....	.....	.....	.....	.....

Series e_2.

.....	.....	.....	.....	2030.7	.....	.....	.....
.....	.....	.....	.....	.....	70.3	.....	.....
.....	.....	.....	.....	2101.0	.....	.....	.....
.....	.....	.....	.....	.....	71.5	.....	.....
.....	.....	.....	.....	2172.5	.....	.....	.....
.....	.....	.....	.....	.....	69.7	.....	.....
.....	.....	.....	.....	2242.2	.....	.....	.....
.....	.....	.....	.....	.....	71.0	.....	.....
.....	.....	.....	.....	2313.2	.....	2314.0	.....
.....	.....	.....	.....	.....	69.5	.....	69.0
.....	.....	.....	.....	2382.7	}	2383.0	}
.....	.....	.....	.....	———	}	———	}71.2×2
.....	.....	.....	.....	———	}71.7×3	2525.3	}
.....	.....	.....	.....	———	}	.....	69.4
.....	.....	.....	.....	2597.8	}	2594.7	.....

Series e_2''.

.....	.....	2031.0	.....	.....	.....	2034.1	.....
.....	.....	.....	71.4	.....	.....	.....	71.4
.....	.....	2102.4	.....	.....	.....	2105.5	.....
.....	.....	.....	72.0	.....	.....	.....	70.6
.....	.....	2174.4	.....	.....	.....	2176.1	.....
.....	.....	.....	67.8	.....	.....	.....	68.9
.....	.....	2242.2	}	.....	.....	2245.0	.....
.....	.....	———	}	.....	.....	.....	72.8
.....	.....	———	}72.7×2	.....	.....	2317.8	.....
.....	.....	———	}	.....	.....	.....	70.8
.....	.....	2387.5	}	.....	.....	2388.6	}
.....	.....	.....	72.2	.....	.....	———	}
.....	.....	2459.7	.....	.....	.....	———	}70.6×2
.....	.....	.....	71.0	.....	.....	———	}
.....	.....	2530.7	.....	.....	.....	2529.7	}

TABLE 34.—*General list of absorption bands in spectra of the double uranyl chlorides at −185° C.*—continued.

Series a_1'.

Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.	$\frac{1}{\lambda}\times10_3$	Interval.	$\frac{1}{\lambda}\times10^3$	Interval.
.....	.....	.....	.....	2036.9	.....	2038.1	.....
.....	.....	.....	.....	.....	70.6	.....	70.3
.....	.....	.....	.....	2107.5	.....	2108.4	.....
.....	.....	.....	.....	.....	70.7	.....	70.7
.....	.....	.....	.....	2178.2		2179.1	.....
.....	.....	.....	.....	———		.....	70.6
.....	.....	.....	.....	———		2249.7	.....
.....	.....	.....	.....	———	71.1×3	.....	72.6
.....	.....	.....	.....	———		2322.3	.....
.....	.....	.....	.....	———		.....	71.2
.....	.....	.....	.....	2391.5		2393.5	
.....	.....	.....	.....	.....	71.9	———	
.....	.....	.....	.....	2463.4	.....	———	70.4×2
.....	.....	.....	.....	.....	70.2	———	
.....	.....	.....	.....	2533.6	.....	2534.3	

Series a_1.

.....	.....	2038.5	.....	.....	.....	.....	.....
.....	.....	.....	71.5	.....	.....	.....	.....
.....	.....	2109.0	.....	.....	.....	.....	.....
.....	.....	.....	71.2	.....	.....	.....	.....
.....	.....	2180.2	.....	.....	.....	.....	.....
.....	.....	.....	70.7	.....	.....	.....	.....
.....	.....	2250.9	.....	.....	.....	.....	.....
.....	.....	.....	71.9	.....	.....	.....	.....
.....	.....	2322.8	.....	.....	.....	.....	.....
.....	.....	.....	71.2	.....	.....	.....	.....
2384.4	.....	2394.0	.....	.....	.....	.....	.....
.....	72.0	.....	72 8	.....	.....	.....	.....
2456.4	.....	2466.8	.....	.....	.....	.....	.....
.....	69.2	.....	70.5	.....	.....	.....	.....
2525.6	.....	2537.3	.....	.....	.....	.....	.....
.....	69.1	.....	71.7	.....	.....	.....	.....
2594.7	.....	2609.0	.....	.....	.....	.....	.....

Series a_2.

2038.1	.....	.....	.....	2044.2	.....	2045.3	.....
.....	70.4	.....	.....	.....	70.7	.....	71.1
2108.5	.....	.....	.....	2114.9	.....	2116.4	.....
.....	70.4	.....	.....	.....	70.0	.....	70.1
2178.9		.....	.....	2184.9	.....	2186.5	.....
———	70.4×2	.....	.....	.....	.....	.....	.....
2319.6		.....	.....	.....	.....	.....	.....

Series a_2''.

2391.9		.....	.....	.....	.....	.....	.....
———	70.7×2	.....	.....	.....	.....	.....	.....
2533.3		.....	.....	.....	.....	.....	.....
.....	74.2	.....	.....	.....	.....	.....	.....
2607.5	.....	.....	.....	.....	.....	.....	.....

VI. THE POLARIZED SPECTRA OF THE DOUBLE CHLORIDES AND DOUBLE NITRATES.

The polarization of the fluorescent light from crystals, first noted by Grailich in 1857,[1] has since been studied by Maskalyne,[2] von Lommel,[3] E. Wiedemann,[4] Sohncke,[5] Schmidt,[6] H. Becquerel,[7] and Pochettino.[8]

With the exception of the work of Becquerel on the ruby, in which low temperatures were employed, the authors cited above dealt chiefly with fluorescence of the usual type, consisting of broad bands. In such cases the most that can be done is to determine the direction of vibration and estimate the proportion of polarized light.

The uranyl salts afford a much more favorable field for such investigations. Well-formed crystals of certain of these salts show a marked pleochroism. When viewed through a Nicol prism their color changes from a yellow-green to a very pale yellowish-white when the plane of the Nicol is turned through 90°. In the case of the double chlorides of uranyl (*i. e.*, $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$; $UO_2Cl_2 \cdot 2KCl + 2H_2O$; $UO_2Cl_2 \cdot RbCl + 2H_2O$; and $UO_2Cl_2 \cdot 2CsCl$), these changes of color are connected with striking and significant variations in the fluorescence and absorption spectra, and this is true also of certain of the double nitrates.

These double chlorides, as has been shown in Chapter V, differ from the other uranyl salts thus far studied in the greater degree of resolution exhibited by their spectra at +20°. The further resolution effected by cooling the crystal to the temperature of liquid air is in general the same for all; *i. e.*, the bands are resolved into doublets the components of which in some cases, particularly noticeable in the absorption spectra, show indications of further complexity. The doublets, moreover, are polarized,[9] the planes of vibration of the components being at right angles to one another, so that two entirely distinct spectra of fluorescence and absorption may be observed by the use of a Nicol prism.

For the study of these remarkable phenomena the apparatus depicted in figure 70 was devised.

Within the collimator of a spectroscope of constant deviation a rhomb of calcite *R* was so mounted as to give two vertically displaced images of the slit, and these by suitable adjustment of the length of the slit could be rendered contiguous without overlapping.

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[1] Grailich, Krystall-optische Untersuchungen, Wien, 1858.

[2] Maskalyne, Proc. Royal Society, XXVIII, p. 479.

[3] von Lommel, Wiedemann's Annalen, VIII, p. 634.

[4] E. Wiedemann, Wiedemann's Annalen, IX, p. 158.

[5] Sohncke, Wiedemann's Annalen, LVIII, p. 417.

[6] G. C. Schmidt, Wiedemann's Annalen, LX, p. 740.

[7] H. Becquerel, Comptes Rendus, CXLIV, p. 671.

[8] Pochettino, Nuovo Cimento (v), 18. 1909.

[9] Nichols and Howes, Proce. Nat. Acad. Sci. 1, p. 444, 1915; and more fully in Phys. Rev. VIII, p. 364. 1916.

The crystal C was mounted before the slit and turned about the axis of the collimator until the planes of vibration of the transmitted light coincided with planes of transmission of the rhomb.

For the study of fluorescence, the light from a carbon arc A, after passage through the condensing lens L, the water-cell W, and a light-filter F, was employed for excitation. The filter was opaque to light of a wave-length greater than 0.45μ, so that the fluorescence appeared on a black background. When absorption spectrographs were required a pale-blue screen was substituted, and the carbon arc was replaced by a 1,000-watt nitrogen-filled tungsten lamp.

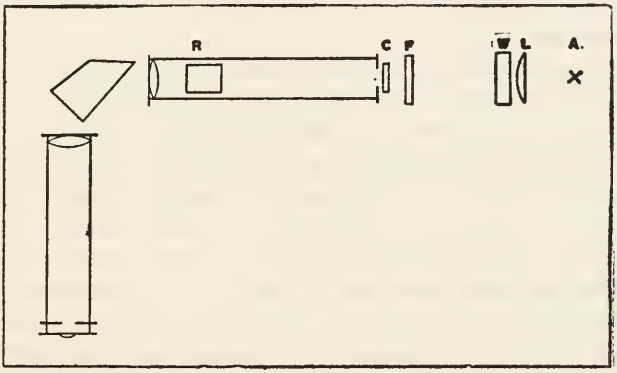

FIG. 70.

Many crystals were produced before any were found which gave complete separation of the two polarized components. A mere inspection of the crystals was not a sufficient criterion; but when transmitted light polarized parallel to one of the planes of vibration of the crystal was used, the presence of only one of the two absorption spectra was found to afford a very delicate test, both for the adjustment of the apparatus and the homogeneity of the crystal. In accordance with the usage adopted we shall call that component of the spectrum due to vibrations in the more transparent direction of the crystal, the *white component*, while the component at right angles to this will be designated as the *green component*. The stronger fluorescence, as might be expected, is that of the green component, since light polarized in that plane is more strongly absorbed.

The four double chlorides upon which observations were made crystallize in triclinic plates. These were so mounted that the flat faces were at right angles to the transmitted light.

The flat faces of the potassium, ammonium, and rubidium uranyl-chloride crystals correspond to the (*c*) crystallographic face, while the flat face of cæsium-chloride crystals corresponds to the (*b*) crystallographic face. The cæsium chloride crystallizes in gypsum-like plates, which were mounted with the longest (*c*) crystallographic axis vertical. Since the plane of polarization of the white light is also vertical within

a degree or two, light vibrating horizontally is, in this arrangement, less absorbed than light vibrating vertically. As to the direction of vibration of the white light within the crystal, it can be said to be more nearly parallel to the (*a*) crystallographic axis than to the (*b*) axis. Rubidium chloride crystallizes in long six sided plates. As mounted, plane polarized light was transmitted most freely when the direction of vibration was parallel to the (*a*) crystallographic axis. Potassium and ammonium chlorides crystallize in thin plates which approximate more nearly the hexagon in form. Examination of the transmitted light with the aid of a Nicol shows that the same relations exist between the directions of vibration and the crystallographic axes as for the rubidium chloride.[1]

Two polarized fluorescence spectra are always present, provided the crystal is mounted as previously described. It is a remarkable fact that these spectra remain unchanged, whether the exciting light is unpolarized or is polarized in a white or green direction, or any other direction. Their character, moreover, appears to be independent of the direction from which the exciting light enters the crystal. This is in agreement with a general principle established by the study of fluorescence spectra,[2] that the character and location of a fluoresecnce band is independent of the nature of the excitation. Changes in the polarized spectra occur, however, as might be expected, if different crystallographic faces are placed at right angles to the axis of the collimator.

Although visual observations were made, the spectra were mapped for the most part from the photographic plates. Occasionally, the fluorescence and a portion of the absorption spectrum could be photographed simultaneously to advantage, but more often different screening and various times of exposure were necessary in order to bring out different regions of the absorption. The exposures varied in time from 30 seconds to an hour.

A STUDY OF TYPICAL GROUPS OF BANDS FROM THE FLUORESCENCE AND ABSORPTION SPECTRA AT +20° C.

In the study of the spectra of the double chlorides described in Chapter V, it has been shown that each group consists of 5 members and that each of these bands is double. Since polarization effects a resolution or separation, we should expect in general to find 5 components in each polarized fluorescence group. In that chapter the bands of one fluorescence group have been designated as B, C, D, E, and A, and the same nomenclature will be employed here.

A typical fluorescence group for each of the four salts is indicated in figure 71. The bands above the horizontal line are the green polarization components (B_g, C_g, etc.); those below, the white polarization

[1] The excellent specimens which were finally utilized in this investigation we owe to the persistent and skillful efforts of Mr. D. T. Wilber.

[2] Nichols and Merritt, Physical Review, series I, 27, p. 373. 1908.

components (B_w, C_w, etc.). The lengths of the bands give an approximate idea of their intensities, although the difference in intensity between a strong C band and a weak A band can not be shown to advantage in such a diagram. The positions of the crests of the bands are taken from the observed values, to be found in table 35, but the width and form of the bands are more or less arbitrary, being the expression of a judgment based on a large number of observations.

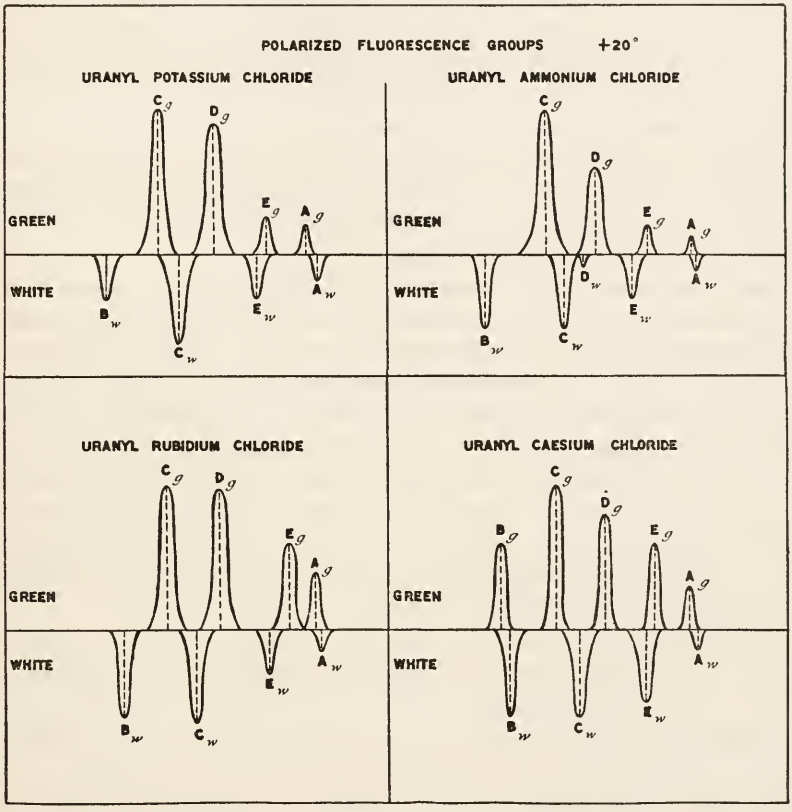

FIG. 71.

From this figure it will be seen that bands C, E, and A of uranyl potassium chloride appear as doublets, polarized at right angles. Band B has no green component visible, but, as will be shown in a subsequent paragraph, at −185° a green component is present, which lies nearer the red than B_w. Bands C_g and C_w are the two components of band C, while no component of band D has been found on the white side. Bands E and A are also well resolved; the white component of band E is of longer wave-length than the green component, while the white components of C and A, and probably of B, are of shorter wave-length than their respective green components.

The uranyl ammonium chloride group shows a strong similarity to the preceding group. All except band B appear as polarized doublets. Components D_w and A_w were discerned only with the greatest difficulty.

The uranyl rubidium chloride group is very similar to the uranyl potassium chloride group. Band B_g is missing, but as in the potassium chloride, there is a $-185°$ component to the red of B_w. Component C_w has a position nearer D_g than has C_w in the preceding spectra. This is also the condition existing in the cæsium-chloride spectrum, and it is possible, since no D_w component is visible in either spectrum, that D_w is very dim, and hidden in C_w.

Uranyl cæsium chloride gives the most satisfactory set of fluorescence bands, since both components of band B are present, and the C, E, and A components are very well separated. It is interesting to note that B_g is of longer wave-length than B_w, as is the $-185°$ component of B_g in the preceding salts.

It has been previously stated that the absorption spectra, like the fluorescence spectra, are composed of series, which begin with the bands which terminate the fluorescence series. The absorption bands which lie nearest the fluorescence region can also be arranged in recurring groups. The absorption series will be designated *b, c, d, e, a;* since they join the B, C, D, E, and A fluorescence series, respectively. The *e* and A series are the strongest in the reversing region, but gradually vanish, while the D series becomes stronger toward the ultraviolet. Figure 72 gives a typical absorption group for each of the four salts. As before, the components above the line belong to the green; those below to the white polarization.

By comparing the uranyl potassium chloride absorption group in figure 72 with the fluorescence group of the same salt in figure 71, it will be seen that there is no b_g component present, as there was no B_g component present, but that c_g, d_g, e_g, and a_g, corresponding to series C_g, D_g, E_g, and A_g are present and that there are no other series represented. Although the relative intensities of the absorption components are almost reversed when compared with the relative intensities of the fluorescence bands, the same spacing exists between the green components of both fluorescence and absorption. In the white polarization group, c_w corresponds, in position, to C_w, and e_w to E_w, while b_w a_w serves both B_w and A_w series in the following way: B_w is the first member of each fluorescence group, while A_w is the band of the preceding group which is nearest to B_w. As the fluoresence intervals of both the A and B series are approximately 83 frequency units, and A_w is 12 units distant from B_w, the reversing band of the a_w series must coincide with the second member of the b_w absorption series, since it is 71 units from the reversing band B_w or b_w. The d_w component is absent, as is D_w, and there are no superfluous series.

The absorption group of the uranyl ammonium chloride is very similar to that of the potassium chloride. Again, the b_g component, like the B_g component, is absent, but the other fluorescence series are represented by absorption series, save that no component of d was found to join the very weak D_w fluorescence band.

Uranyl rubidium chloride shows a grouping analogous to that of the potassium and ammonium chloride, while the uranyl cæsium chloride group is only slightly different.

A b_g series is present, which is properly related to the B_g series, so that b_g and b_w are the same relative positions as are B_g and B_w.

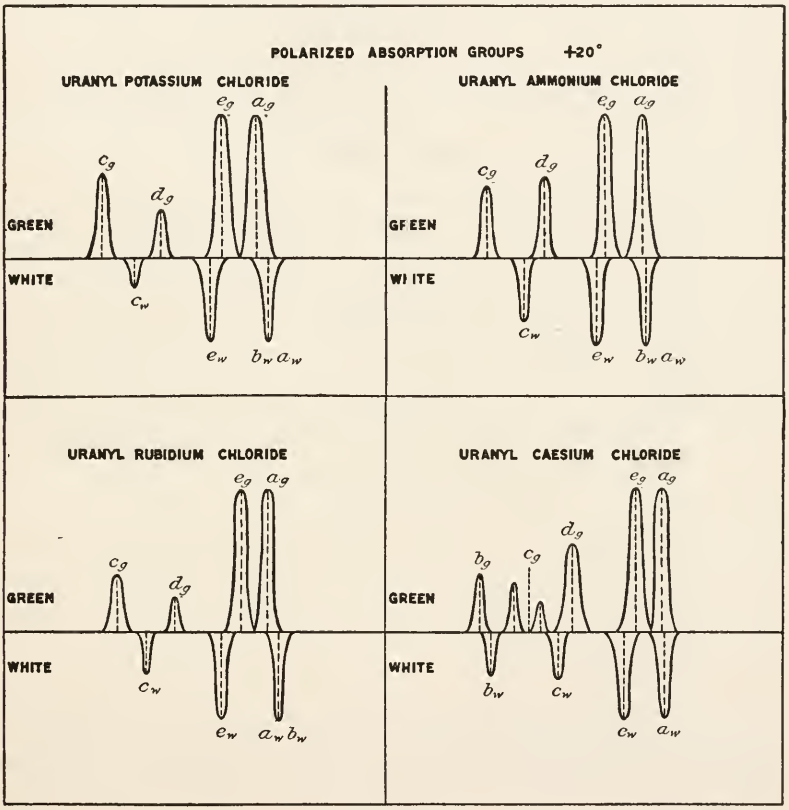

Fig. 72.

No green polarized component joins the C_g component. The dotted line shows where an absorption component would have to be placed to have the proper relation, according to our theory. The c_g band is evidently complex. c_w is present, however, as a single band, and the d, e, and a components occupy positions which agree with their corresponding fluorescence components. b_w and a_w are here separate.

A DETAILED STUDY OF THE RELATION BETWEEN FLUORESCENCE AND ABSORPTION SERIES.

In figure 73 are indicated 2 complete fluorescence groups and 2 complete absorption groups for each of the 8 spectra. The remarkable fact is that although no observed fluorescence bands have been omitted which fall within the frequency numbers plotted, *each fluorescence series has its properly related absorption series*, and with the exception of the complex C_g series of the cæsium chloride not a superfluous

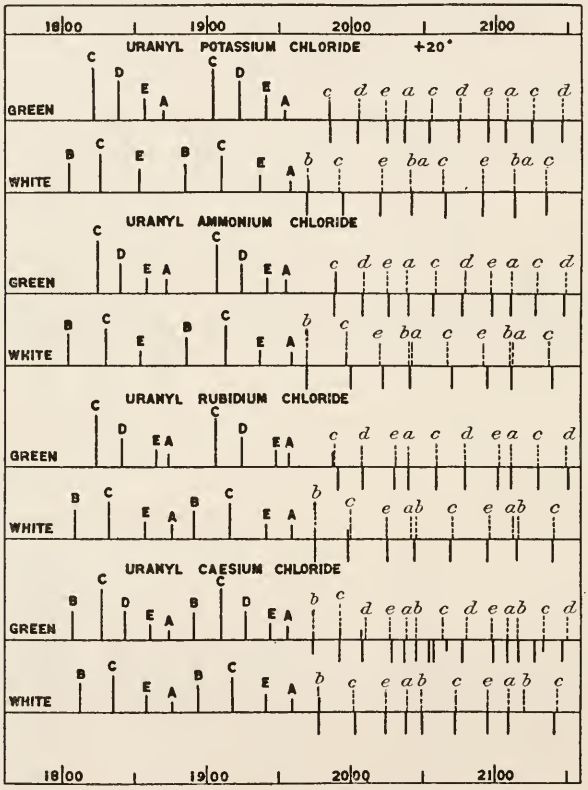

FIG. 73.—Polarized bands of fluorescence and absorption; four contiguous groups showing the relation between the green and white components at +20°. Dotted lines show computed positions of absorption bands. Solid lines above the base indicate fluorescence; below the base, absorption.

absorption series is present. Fluorescence bands are designated by the solid lines above the horizontal, and absorption bands by the solid lines below the horizontal. The dotted lines above the absorption bands represent the hypothetical positions of absorption bands, computed in the following manner:

The average interval for the series in question was computed from all available observations on the bands which belong to it, carefully weighted. A hypothetical position for the band in the reversing group was then found by adding this interval to the average of the observations on the position of the preceding band of the series. This hypo-

thetical position was taken as the starting-point of the corresponding absorption series, the hypothetical positions of the subsequent members being found by addition of the weighted average for the observed interval of that series.

By reference to figure 73 and to tables 35 and 37, the reader can note the general agreement between observed and calculated positions; also the occasional discrepancies. In the spectra of uranyl ammonium chloride and uranyl rubidium chloride for example, the B_w and A_w series are spaced at such an interval that a_w and b_w can not coincide, as will be seen from figure 73. The observed $b_w a_w$ bands occupy positions between the assumed positions of the *b* and *a* series, which tends to show that the *ba* band is a narrow doublet. The fact that a few of the observed absorption bands do not appear to be in their proper places can be readily explained when it is remembered that there is sufficient experimental evidence to lead to the belief that many of the absorption bands are doublets, consisting of a strong and a weak component. The breaks in a few of the absorption series, as in the e_g and a_g series of the uranyl ammonium chloride, are undoubtedly due to the sudden increase in strength of one component, accompanied by a corresponding decrease in the other component.

Table 35 contains the observed positions of all the fluorescence and absorption bands at +20°, measured in our determinations of the spectra of the four salts. Figure 73 is a map of only the central portion, extending, as already stated, two groups into the fluorescence on the one side and two groups into the absorption on the other.

TABLE 35.—*Polarized series at +20° C.*

URANYL POTASSIUM CHLORIDE.

Fluorescence.							
Green component.				White component.			
C.	D.	E.	A.	B.	C.	E.	A.
.....	1756.3	1774.6	1788.9	.....	.....	1770.9	.....
1821.0	1838.6	1856.9	1871.2	1804.2	1827.2	1853.5	.....
1903.1	1922.0	1940.6	1955.2	1887.1	1909.6	1937.5	1958.0
1984.6	.....	.....	.....	1970.1	1992.0	.....	.....

Absorption.						
Green component.				White component.		
c.	*d.*	*e.*	*a.*	*ba.*	*c.*	*e.*
1985.7	2004.4	2024.7	2036.7	1968.1	1994.4	2019.8
2054.2	2073.8	2094.7	2106.7	2039.6	2064.8	2090.7
2125.4	2145.5	2165.9	.....	2111.0	2134.9	2160.8
.....	.....	.....	.....	2179.1	.....	.....
.....	2287.8	.....	2247.7	.....	.....	.....
.....	2359.0	.....	.....	2398.1	.....	.....
.....	.....	.....	2602.4	.....	.....	.....
2624.0	.....	.....	2673.8	.....	2635.0	.....
2695.4	.....	.....	2743.5	.....	.....	.....

TABLE 35.—*Polarized series at 20° C.*—continued.

URANYL AMMONIUM CHLORIDE.

Fluorescence.							
Green component.				White component.			
C.	D.	E.	A.	B.	C.	E.	A.
1742.1	1756.4	1775.8	1790.0	.....	1748.4	1770.9	.....
1824.0	1840.3	1857.6	1874.1	1804.2	1829.6	1853.8	.....
1907.0	1923.6	1941.6	1957.8	1886.8	1912.9	1937.0	1959.0
1990.0	.....	.....	.....	1970.6	.....	.....	.....

Absorption.						
Green component.				White component.		
c.	*d.*	*e.*	*a.*	*ba.*	*c.*	*e.*
1988.5	2007.9	2026.5	2039.9	1970.5	1999.8	2022.4
2057.3	2077.3	2098.1	2110.9	2042.6	2070.2	2094.7
2128.1	2146.9	2169.8	2182.3	2114.1	2140.5	2166.0
.....	2218.1	2240.1	2256.8	2185.0	.....	.....
.....	2289.7	2313.2	2327.7	.....	.....	2311.8
.....	2360.8	2383.3	2399.2	.....	.....	2381.8
.....	2431.4	2455.8	.....			
.....	2500.8	2525.9	.....			
.....	2571.4	.....	.....			
2623.3	.....	.....	.....			

URANYL RUBIDIUM CHLORIDE.

Fluorescence.							
Green component.				White component.			
C.	D.	E.	A.	B.	C.	E.	A.
1739.1	1757.6	1781.9	.....	.....	1750.6	1774.7	1793.6
1822.7	1840.9	1865.3	1973.7	1808.8	1832.4	1858.0	1875.5
1905.0	1923.9	1948.8	1956.9	1891.1	1916.4	1941.6	1959.5
1986.9	.....	.....	.....	1975.3	.....	.....	.....

Absorption.						
Green component.				White component.		
c.	*d.*	*e.*	*a.*	*ab.*	*c.*	*e.*
1991.2	2008.4	2030.0	2040.4	1973.7	1999.2	2024.3
2059.3	2079.4	2101.7	2111.5	2043.8	2069.1	2094.7
2130.4	2151.0	.....	.....	2114.9	2140.2	2165.9
.....	.....	.....	.....	2148.8	2209.5	.....
.....	2294.1	.....	.....	2253.8	.....	.....
.....	2364.1	.....	.....	.....	.....	.....
.....	2434.9	.....	.....	.....	.....	.....
.....	2507.5	.....	.....	.....	.....	.....
.....	2579.3	.....	.....	.....	.....	.....
2629.5	.....	.....	.....	.....	.....	2590.7
				2677.4	.....	.....

TABLE 35.—*Polarized series at 20° C.*—continued.

URANYL CÆSIUM CHLORIDE.

Fluorescence.								
Green component.					White component.			
B.	C.	D.	E.	A.	B.	C.	E.	A.
.....	.....	1761.2	1778.1	1789.9	1729.8	1751.3	1775.6	1793.4
1807.3	1827.2	1843.3	1860.8	1873.7	1812.3	1835.2	1858.0	1875.8
1891.1	1909.9	1927.5	1944.4	1956.2	1894.3	1917.9	1941.4	1958.1
1973.6	1992.0	.....	.....	.....	1978.0	2000.4	.....	.....

Absorption.								
Green component.					White component.			
b.	*c.*	*d.*	*c.*	*a.*	*b.*	*c.*	*e.*	*a.*
1973.9	1991.6	2007.4	2028.6	2036.4	1978.2	2002.8	2024.5	2037.1
2045.6	2057.6	2076.4	2098.6	2107.6	2049.0	2072.1	2094.9	2107.9
	2065.7	.....	.....	.....	.....	2140.9	2164.9	2179.1
2116.4	2127.9	2145.2	2170.1	2179.1	.....	2212.9	2235.6	.....
	2133.1	.....	.....	.....				
2187.0	2198.3	2214.6	.....	.....				
	2202.2	.....	.....	.....				
.....	.....	2284.1	.....	.....				
.....	.....	2355.4	.....	.....				
.....	.....	2426.9	.....	.....				
2467.9	.....	2496.3	.....	.....				
2538.7	.....	2567.4	.....	2602.1				
.....	2624.0	2637.1	.....	2673.8				
.....	2696.1	.....	.....	.....				

THE EFFECT OF LOW TEMPERATURES ON THE RESOLUTION AND POSITION OF THE BANDS.

It has been shown in Chapter V that low temperature tends to narrow all the bands in the spectra of the double chlorides, to resolve them into doublets, and to produce certain shifts in their position. These temperature shifts were explained by assuming that the bands at +20° are close overlapping doublets, the stronger components of which are weakened by lowering the temperature, while the weaker components are strengthened. Such shifts occur in all of the polarized spectra here under consideration and the same explanation is applicable. They will be considered in detail in a later paragraph.

In table 36 are recorded the observed positions of the fluorescence and absorption bands in the two polarized components at −185°.

Figure 74, like figure 73, is a map of four contiguous groups, two of fluorescence and two of absorption, inserted to facilitate the comparison of the green and white components as regards the location of the bands. Since the arrangement repeats itself from group to group, it is unnecessary to include the outlying regions toward the red and toward the violet.

TABLE 36.—*Polarized series at −185° C.*

URANYL POTASSIUM CHLORIDE.

Fluorescence.								
Green component.					White component.			
C.	D.	E.	A.	A′.	B.	C.	E.	A.
1738.4	.....	.....	1785.4	1797.9	.....	1741.3	1771.9	1786.4
1820.5	1842.3	1858.1	1868.8	1881.7	1807.3	1826.2	1854.9	1870.9
1903.3	1926.0	1940.8	1953.5	1966.6	1891.4	1911.7	1938.5	1954.7
1985.7	.....	.....	.....	.....	1975.5	1996.0	.....	.....

Absorption.							
Green component.				White component.			
c.	*d′.*	*d.*	*d″.*	*c.*	*b.*	*e.*	*a.*
.....	.....	2010.5	.....	2000.4	2114.2	2021.0	2041.2
2058.0	2076.6	.....	2086.4	2067.8	2184.8	2092.7	2112.2
2128.1	2146.8	2152.9	2157.5	2137.7	2257.8	2164.0	2182.6
2199.3	2218.7	2222.2	2228.8	2207.5	.....	.....	2252.7
.....	2289.9	.....	2301.5	.....	.....	.....	.....
.....	.....	.....	2371.1	.....	.....	.....	.....
.....	.....	.....	2440.8	.....	2541.9	.....	.....
2485.7	.....	.....	2512.3				
e.	*e′.*	*a.*	*c′.*				
2024.3	2028.4	2036.2	.....				
2094.2	2099.1	2106.6	2124.0				
2164.5	2169.7	2177.8	2193.5				
.....	2241.4	2248.5	.....				
.....	.....	.....	.....				
.....	2384.9	.....	.....				
.....	.....	.....	.....				
.....	2525.3	2532.9	.....				

URANYL AMMONIUM CHLORIDE.

Fluorescence.								
Green component.					White component.			
C′.	C.	D.	E.	A.	B′.	B.	C.	C′.
1738.5	1744.6	.....	.....	.....	.....	.....	1751.2	1777.5
1821.2	1828.0	1843.5	1857.7	1783.6	1803.8	1810.1	1835.5	1861.6
1905.1	1911.7	1928.2	1941.0	1868.1	1888.4	1894.1	1919.7	1946.7
1988.9	1994.8	2012.5	2023.5	1952.4	1972.9	1978.2	2004.2	.....

Absorption.								
Green component.					White component.			
c.	*d.*	*e.*	*a.*	*a′.*	*b.*	*c.*	*e.*	*e′.*
.....	.....	2023.6	2037.9	2044.2	.....	.....	2018.8	2030.3
2063.0	2085.8	2094.9	2108.8	2115.5	.....	.....	.....	.....
2066.0	.....	.....	.....	.....	2049.4	2077.6	.....	2102.2
2135.5	2156.6	2166.5	2181.1	.....	2121.2	2148.6	.....	2174.0
2138.4	.....	.....	.....	.....	2192.0	2217.8	2233.1	.....
2205.1	2227.9	2238.6	2249.7	.....	2263.8	2287.8	2302.8	.....
2208.7	.....	.....	.....	.....	2334.8	2359.0	.....	.....
2276.6	.....	.....	2321.5	.....				
2279.5	.....	.....	.....	.....				

TABLE 36.—*Polarized series at −185° C.*—continued.

URANYL RUBIDIUM CHLORIDE.

Fluorescence.							
Green component.				White component.			
B.	C.	D.	A.	B.	C.	A.	
.....	1746.4	.....	.....	.....	1755.0	.....	.....
1804.7	1828.8	1845.7	1874.8	1812.4	1837.2	1879.2	.....
1887.9	1912.0	1929.9	1958.9	1895.9	1920.9	1962.3	.....
1971.4	1994.2	2013.7	.....	1979.0	2004.6	.....	.....

Absorption.							
Green component.				White component.			
b.	*c'.*	*c.*	*d''.*	*b.*	*c.*	*e.*	*e'.*
2045.0	.....	2066.1	.....	.....	2004.8	2030.5	.....
2115.5	.....	2136.8	.....	2050.4	2076.2	2100.2	.....
2187.2	2200.7	2207.5	2223.0	2122.2	2146.6	2172.0	.....
.....	2272.7	2279.5	2294.1	2192.0	2216.3	.....	2238.1
.....	.....	2350.7	2362.9	2263.0	.....	.....	2309.5
.....	.....	2420.5	2435.5	2333.7	2359.0	.....	2378.0
.....	2485.1	2491.3	2504.4	.....	.....	.....	2451.0
2541.3	.....	2561.5	2576.3	2478.3	2498.1	2526.5	.....
				2548.4	2570.0	.....	.....
d.	*d'.*	*a'.*	*a.*				
2016.7	.....	2035.8	.....				
2085.5	.....	2108.4	.....				
2159.8	.....	.....	.....				
2229.2	2233.9	2246.7	2254.3				
.....	2305.0	.....	2325.8				
2369.1	2375.0	2391.6	.....				
.....	2446.2	2463.1	.....				
.....	2515.4	2532.9	2537.4				

URANYL CÆSIUM CHLORIDE.

Fluorescence.								
Green component.					White component.			
C.	D'.	D.	E.	A.	B.	C.	E.	A.
1750.7	.....	.....	.....	1794.1	.....	1757.8	.....	1794.9
1834.2	1847.1	1852.3	1866.7	1878.0	1816.6	1841.3	1863.9	1879.0
1916.8	1930.5	1935.8	1950.3	1962.1	1899.8	1924.6	1947.0	1963.1
1997.4	2013.7	2019.0	.....	.....	1983.6	2007.8	.....	.....

TABLE 36.—*Polarized series at −185° C.*—continued.

URANYL CÆSIUM CHLORIDE—*continued.*

Absorption.							
Green component.					White component.		
b.	*b′.*	*c.′*	*c.*	*c″.*	*ba.*	*c.*	*e.*
2050.8	.....	2063.6	.....	.....	.....	2009.6	2033.4
2122.2	2126.8	2134.5	2140.9	.....	2050.8	2081.4	2103.9
2192.7	.....	2204.4	2211.9	2218.5	2122.2	2152.9	2174.9
2262.4	2267.1	2274.8	2280.5 2284.7	2289.4	2192.8	2222.8	2245.0
2333.7	2337.5	2345.8	2354.0	2359.0	2262.4	2294.1	2317.0
2403.8	2409.6	.....	2422.5 2426.6	2431.3	2333.9	2366.3	2386.0
2475.2	2482.6	2489.4	2492.5 2495.6	2500.6	2404.1	2435.2	2458.2
2545.2	.....	2561.5	2566.1	2572.7	.....	2505.0	2529.1
2615.7	2621.2	2631.6	2635.4	2644.8	.....	.....	.....
.....	2695.1	2701.2	2707.1	.....	.....	2646.9	.....
d′.	*d.*	*e′.*	*e.*	*a.*			
.....	2021.0	.....	2035.8	2044.6			
.....	2091.6	.....	2107.0	2115.1			
.....	2163.1	.....	2178.2	2184.8			
2227.5	2233.4	2238.6	.....	2257.8			
2299.1	.....	2310.5	2321.3	2327.7			
2368.8	2378.7	2382.7	2394.1	2400.4			
2441.4	2449.2	.....	2464.9	2467.9			
2510.0	2520.2	2524.0	2534.2	2541.3			

As in these spectra at +20°, so at −185° we find the D bands only in the *green* component, the B bands chiefly in the *white* component.

In the white component, at both temperatures, B, C, and A lie toward the violet, E toward the red. At −185°, B is doubled in the uranyl ammonium chloride, D in the uranyl chloride.

To aid in the direct comparison of the spectra at the two temperatures, they are plotted together in figure 75, in which diagram may be seen the direction of the shift for each series of the two components.

The shift is nearly always toward the violet, the only exceptions being the A_g and a_g series and possibly the A_w series in uranyl potassium chloride (see fig. 74), the e_g and ϵ_g series of uranyl ammonium chloride and the A_y series of the latter salt. The change is greatest in uranyl cæsium chloride and least in the potassium double chloride.

In general the fluorescence bands shift in the same direction and by the same amount as the related absorption bands, but there are some puzzling exceptions to this rule to be considered in a following section.

The increased resolution of the spectra upon cooling shows itself in the doubling of many bands which appear single at +20°, an effect particularly noticeable in the absorption spectra. (See plate 1, *c.*) Thus the c_g series of the potassium salt tends to double at 2,058.0

and becomes clearly double at 2,128.1 and 2,199.3. The d_y and e_g series of the same salt are doubled and the ba series of $+20°$, which was assumed from the relations of the spectrum to be an unresolved doublet, is separated into a b_w and an a_w series at $-185°$. Other examples of doubling may be noted in the case of C_g, c_g, a_g, and B_w of uranyl ammonium chloride, a_g, a_w, and b_w of the rubidium salt, and b_w, D_g, and d_g of the cæsium salt.

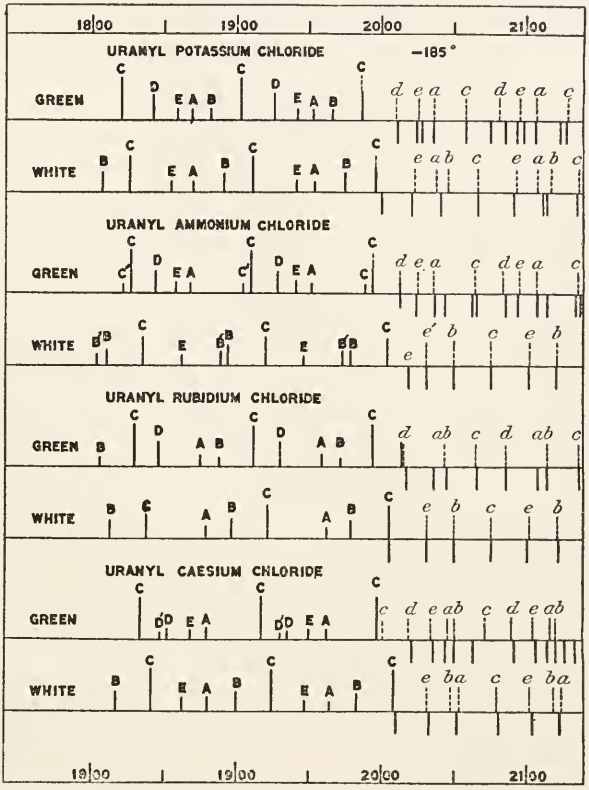

FIG. 74.—Polarized bands of fluorescence and absorption; four contiguous groups showing the relation between the green and white components at −185°. Dotted lines show computed positions of absorption bands; solid lines above the base indicate fluorescence, below the base absorption.

ON THE FREQUENCY INTERVALS OF FLUORESCENCE AND ABSORPTION.

During the preliminary study of the fluorescence and absorption of uranyl ammonium chloride described in Chapter V, the symmetry of the spectrum was such as to lead to the suspicion that the various homologous series would be found to have the same constant-frequency interval. The final tabulation of results, however, after many redeterminations of what seemed to be discordant values, showed that while the departures from uniformity were in general scarcely larger than the errors of observation, they were to some extent systematic and indi-

cated slightly different values for the various series. The C bands in particular, which were a composite of what in these later studies we have designated as C_y and C_w of the polarized spectrum, were found to have an unquestionably smaller interval than the other series of the group.

It will be seen from table 37 that this is true for both C_g and C_w in the case of all four salts at +20° and that with the possible exception of A_w, which is an exceedingly feeble component, visible only in two of the salts and very difficult of determination; all other series are very

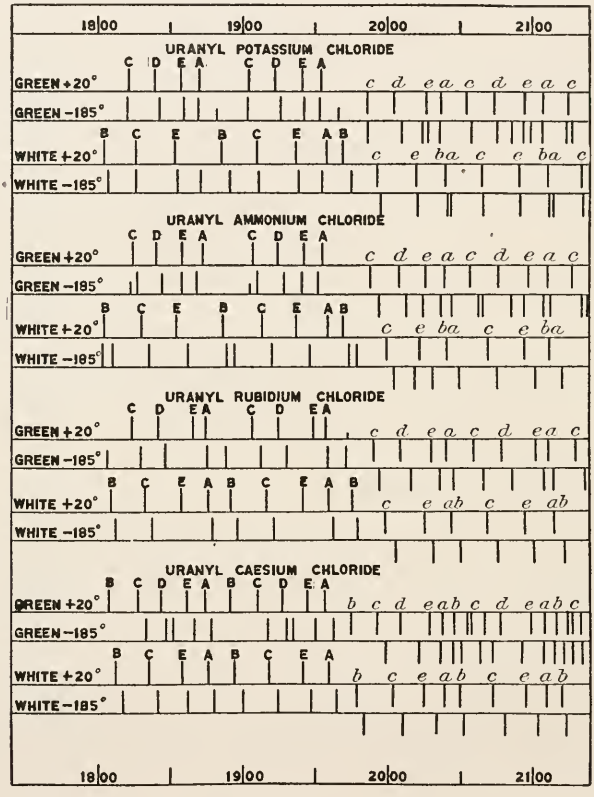

Fig. 75.

nearly of the same interval, not only in the same salt but in all the salts. When, however, we make further averages of the average intervals from table 37, taking the mean of all green components of fluorescence, then of all white components, for each salt separately, and do the same for the absorption intervals, we find an approach to systematic arrangement which is suggestive if not altogether conclusive. (See table 37.)

Both components of the fluorescence spectrum show an average interval in the inverse order of the molecular weights, and while the absorption series do not give so decisive an indication the salts of lesser

molecular weight, NH_4 and K show again a longer interval than do Rb and Cs. Averaging *by series* affords no such direct indication as to differences of interval, as will appear from table 38.

It will be noted that while the averages for the green and white components of fluorescence are in very close agreement at +20° and also at −185°, there is a difference of about 0.5 between the averages for +20° and those for −185°; also that the interval is greater for each individual series at −185° than at +20°, with the single exception of e_w. This difference does not appear, however, in the case of the absorption intervals.

TABLE 37.—*Average frequency intervals, +20° C. and −185° C.*

Fluorescence series.									
Green component.					White component.				
Series.	K	NH_4	Rb	Cs	Series.	K	NH_4	Rb	Cs
B_g....	.....	.....	.....	82.9	B_w...	83.0	83.4	83.6	82.9
C_g....	81.9	82.8	82.2	82.6	C_w...	82.1	82.9	83.3	82.8
D_g....	83.0	83.5	83.1	83.3	.....	.....	.....	.....	.....
E_g....	83.2	83.3	83.5	83.3	E_w...	83.5	83.1	83.5	83.1
A_g....	83:4	83.8	83.2	82.9	A_w...	.....	.....	82.9	82.4
Absorption series.									
Series.	K	NH_4	Rb	Cs	Series.	K	NH_4	Rb	Cs
b_g.....	.....	.....	.....	70.5	b_w...	71.5	71.3	70.4	70.8
c_g.....	71.3	70.7	71.2	70.6	c_w...	71.3	70.3	70.0	70.5
d_g....	71.1	70.5	70.2	70.5	.....	.....	.....	.....	.....
e_g.....	70.8	70.8	71.7	71.0	e_w...	70.4	71.7	70.8	70.4
a_g....	70.7	71.5	71.1	70.8	a_w...	71.5	71.3	70.4	71.4

Average frequency intervals, −185° C.

Fluorescence series.									
Green component.					White component.				
Series.	K	NH_4	Rb	Cs	Series.	K	NH_4	Rb	Cs
B_g....	84.0	.....	83.4	.....	B_w...	84.1	84.1	83.2	83.6
C_g....	82.5	83.4	82.6	82.2	C_w...	84.8	84.4	83.9	83.3
D_g....	83.7	84.4	83.9	83.3	.....	.....	.....	.....	.....
E_g....	83.3	83.2	.....	83.6	E_w...	83.0	.....	.....	83.1
A_g....	84.1	84.4	84.1	84.1	A_w...	84.0	.....	83.1	84.1
Absorption series.									
Series.	K	NH_4	Rb	Cs	Series.	K	NH_4	Rb	Cs
b_g.....	.....	.....	70.9	70.5	b_w...	71.3	71.3	70.8	70.6
c_g.....	71.5	70.9	70.7	70.8	c_w...	69.8	70.6	70.3	70.7
d_g.....	70.3	71.1	71.3	71.4	.....	.....	.....	.....	.....
e_g.....	71.8	71.5	.....	71.0	e_w...	71.4	70.7	71.1	70.9
a_g.....	71.0	70.9	70.6	71.1	a_w...	70.4	.....	.....	70.6

TABLE 37.—*Average frequency intervals, +20° C. and 185° C.*—continued.

General averages of intervals (by salts).

	NH_4.	K.	Rb.	Cs.
Fluorescence.				
Green +20° and −185°...	83.60	83.25	83.25	83.19
White +20° and −185°...	83.78	83.43	83.42	83.16
All fluorescence.....	83.69	83.34	83.33	83.17
Absorption.				
Green +20° and −185°...	70.99	71.07	70.96	70.74
White +20° and −185°...	71.02	70.96	70.55	70.70
All absorption.....	71.00	71.01	70.75	70.72

TABLE 38.—*General averages of intervals (by series).*

Series.	Green. +20°	Green. −185°	Av.	Series.	White. +20°	White. −185°	Av.
Fluorescence.							
Eg....	83.33	83.37	83.35	Ew...	83.37	83.05	83.17
Bg....	.....	83.70	83.70	Bw...	83.23	83.75	83.49
Ag....	83.26	84.18	83.72	Aw...	82.80	83.73	83.74
Dg....	83.23	83.83	83.53	Dw...	.....	.....	.....
Cg....	82.38	82.68	82.53	Cw...	82.78	84.10	83.44
Av....	83.05	83.54	83.37	Av....	83.05	83.66	83.36
Absorption.							
	+20°	−185°	Av.		+20°	−185°	Av.
e_g.....	71.07	71.40	71.23	e_w....	70.82	71.02	70.90
b_g.....	.....	.....	.....	b_w....	71.00	71.00	71.00
a_g.....	71.02	70.90	70.96	a_w....	70.90	70.70	70.80
d_g.....	70.58	71.02	70.75	d_w....	.....	.....	.....
c_g.....	70.95	70.98	70.96	c_w....	70.50	70.35	70.42
Av....	70.90	71.07	70.97	Av....	70.81	70.77	70.78

On the other hand, differences so large are not to be regarded as errors of observation, it being possible to determine the average interval of any series, excepting possibly A_g and A_w, which are very weak and rather vague, within about 0.2. It does not follow, however, that the bands are really thus irregularly placed. The discrepancies are due rather to the fact that resolution is not equally complete in all portions of the spectrum and that on cooling the crystal structure was more or less disturbed and the polarization always much less complete. The anomalous values above 84 frequently observed at −185° (see table 37) are probably due to varying components of the opposite polarization superimposed on the bands in question and producing a false

shift. Thus, for example, the position of C_w would be modified by the presence of the overlapping of D_g or C_g; D_g by C_g, etc. In short, it is probable that if observations could be had on crystals which at $-185°$ preserved their structure, the difference in interval between $+20°$ and $-185°$ would disappear.

THE INFLUENCE OF MOLECULAR WEIGHT UPON THE POSITION OF BANDS.

While some doubt may be felt as to the validity of the suggestion, based upon the averages presented in the foregoing paragraphs, that there is a relation between frequency intervals and the molecular weight, there can be no question as regards the influence of molecular weight upon the position of the bands.

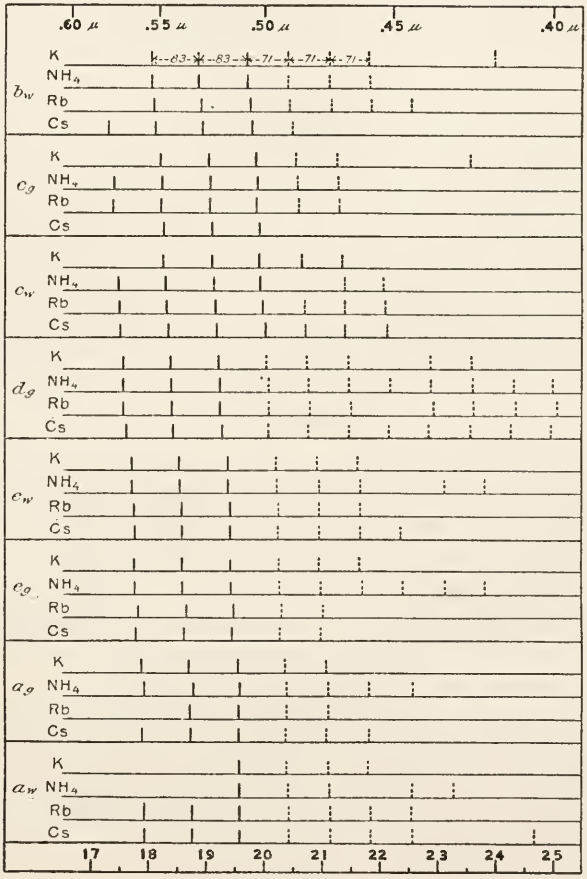

FIG. 76.

If we select a typical region in the spectrum and arrange the bands belonging to a single group as in table 39, we find a general drift of the various bands toward the violet as we pass from salt to salt in the order K, NH_4, Rb, Cs.

The same drift occurs quite systematically throughout the entire fluorescence and absorption spectrum, as may be seen from figure 76. In this chart such of the fluorescence and absorption series as are present in all four salts at +20° are plotted on the frequency scale. The solid lines represent observed fluorescence bands; the dotted lines represent observed absorption bands; no hypothetical values are indicated. The order of the salts is the same as in table 39 and follows

TABLE 39.

	Green polarization, 185°.				White polarization, 185°.			
	C_g.	D_g.	E_g.	A_g.	B_w.	C_w.	E_w.	A_w.
K.....	1903.3	1842.3	1940.8	1868.8	1891.4	1911.7	1854.9	1870.9
NH_4...	1911.7	1843.5	1941.0	1868.1	1894.1	1919.7	.....	.....
Rb....	1912.0	1845.7	.....	1874.8	1895.9	1920.9	.....	1879.2
Cs....	1916.8	1852.3	1950.3	1878.5	1899.8	1924.6	1862.5	1879.9

that given by A. E. Tutton in his Treatise on Crystalline Structure and Chemical Constitution (London, 1916). He found for both single and double salts of the alkali metals that several of their optical properties, such as refractive index, etc., follow the order of the molecular weights, but that in the ammonium salts the NH_4 radical often acts as if it were much heavier than the combined weights of its components would indicate, so that its position is quite close to rubidium and sometimes on the side toward cæsium. It will be observed that there are several examples of this in figure 76, particularly in the case of the C_g series.

SUMMARY.

(1) The four double chlorides, uranyl ammonium chloride, uranyl potassium chloride, uranyl rubidium chloride, and uranyl cæsium chloride, crystallize in the triclinic system. The crystals are pleochroic and their fluorescence spectra and absorption spectra are polarized.

(2) The spectra differ from those of other uranyl compounds thus far examined in that both in the fluorescence and absorption regions each band is resolved at +20° C. into a group of five bands forming homologous series of constant frequency interval.

(3) The structure of the fluorescence spectrum is essentially the same in the different salts, the spacing of the bands of each group repeating itself in the successive groups, excepting in the reversing region, the appearance of which is modified by the overlapping of fluorescence and absorption.

(4) Each of the five bands which constitute a group is a doublet, the two components of which are polarized at right angles to one another.

(5) The frequency interval is the same or nearly the same for each series in a given salt.

(6) Variations in the average interval for the four salts are scarcely greater than the errors of observation, but there are indications of a very slight decrease of interval with increase of molecular weight, and this applies alike to fluorescence and absorption series.

(7) The position, in the spectrum, of a given band varies slightly but systematically with the molecular weight of the salt. The order of diminishing wave-lengths is K, NH_4, Rb, Cs; the shift from K to Cs being of the order of 5 Å. U. This shift is in the same direction—from red toward violet—for all the homologous series and of the same size within the errors of observation.

(8) Cooling to the temperature of liquid air produces the usual narrowing of bands, apparent shifts of position, and apparent changes of interval, all of which changes are explained by the relative enhancement or diminution of components of the bands.

VII. THE NITRATES AND PHOSPHATES; INFLUENCE OF WATER OF CRYSTALLIZATION AND OF CRYSTAL FORM.

I. URANYL NITRATE AND EFFECT OF WATER OF CRYSTALLIZATION.

The spectra of the different uranyl salts are so similar in their general characteristics that we can scarcely doubt that the nature of these spectra is chiefly determined by the radical UO_2. Apparently the uranyl radical contains a group of electrons whose arrangement is such as to permit of vibrations that give this type of spectrum; and although UO_2 is not stable in the chemical sense and must be combined with some acid in order to form a stable compound, yet the effect of the acid radical is merely to modify the constants of this vibrating system in the UO_2 radical without changing the type of vibration.

It is natural to expect that the addition of water of crystallization would produce a similar effect, and it is our intention to present in this section of Chapter VII the results of a study of the influence of water of crystallization upon the fluorescence and absorption spectrum in the case of uranyl nitrate. The nitrate is particularly suited for such an investigation because of the fact that several different hydrates are formed. The crystals grown from a water solution contain 6 molecules of water. In an acid solution crystals are formed with 3 molecules of water. In both cases crystals may be obtained which are large enough to permit of observations being made with a single crystal. By methods described later, small crystals containing only 2 molecules of water are readily obtained. It is a matter of some difficulty to push the dehydration further, but specimens have been prepared for us by Mr. D. T. Wilber which we have reason to believe are either anhydrous or formed of a mixture of the anhydrous salt and the monohydrate.

The fluorescence of the nitrate, like that of the other uranyl salts, with the exception of the double chlorides, the resolution of the bands of whose spectra into groups of five at $+20°$ has been described in Chapter VI, is unresolved at ordinary temperatures. Careful spectrophotometric measurements of what appear to be unresolved bands reveal, however, indications of overlapping components, as has already been shown in Chapter III.

At the temperature of liquid air the resolution into narrow bands characteristic of the uranyl spectra in general takes place, and it is to these resolved spectra that the following discussion refers.

In the case of the hexahydrate, wave-lengths were in most cases determined photographically. Visual observations, however, were also made, although these could not be extended throughout the whole spectrum. The agreement between measurements made by the two methods was surprisingly good. In the case of weak bands lying near

to bands of great intensity the visual observations were found to be best. The results given for the fluorescence spectra of other hydrates and for the anhydrous salt are based upon visual observations exclusively.

The Hexahydrate: $UO_2(NO_3)_2+6H_2O$.

The hexahydrate crystallizes in the rhombic system with the axial ratio $a:b:c=0.6837:1:0.6088$. The crystals were grown in the form of plates by using a water solution whose depth was equal to the thickness of the plate desired. Single crystals as large as 15 mm. in diameter were obtained with relatively little difficulty. All of the results here discussed are based upon observations made with single crystals.

In selecting the data to be used in taking a final average, each negative was carefully studied and measurements that seemed for any reason doubtful were discarded. The elimination of doubtful observations was made without reference to the agreement or lack of agreement between the different measurements, and was, in fact, completed before the measurements of the different negatives were compared. About 40 negatives were used, although the number for any one line was rarely more than 10.

The errors of calibration of the spectrograph and spectrometer can hardly exceed 1 Å. U., except perhaps in the extreme red end of the spectrum. The uncertainties due to the faintness of certain bands, to their finite width, and to photographic broadening are more difficult to estimate and undoubtedly differ greatly with the character of the band and its position in the spectrum. In the case of the sharper bands of moderate intensity we feel that the averages that are here tabulated are reliable within 1 Å. U. In other words, the reciprocal wave-lengths are accurate to within about 0.02 per cent. For the faint or hazy bands the possible error is undoubtedly much greater.

Of the 55 fluorescence bands observed, 46 can be arranged in 9 series, as tabulated below, the frequency interval being nearly constant in each series. Two of the remaining bands have the same interval, and apparently form part of a series whose other members were too weak to detect. The 7 bands that do not fall in any series arrangement are all extremely weak, and since in most cases they are recorded only once, their existence is subject to considerable doubt. Estimates are given in table 40 of the intensities of the different bands and of the reliability of the measurements. In some cases the series seem to extend into the region of absorption, and in such cases the absorption bands that seem to form part of the series are also given.

The data for series B, D, E, and F, which are made up of the stronger bands and those of medium intensity, are undoubtedly the most reliable. The values of the average interval between bands in these series are 86.0, 85.8, 85.9, and 86.1 respectively. In taking these averages,

the first band in the case of series D and E has been left out of consideration on account of its relative uncertainty. For the other series the interval, although less certain, has nearly the same value. It will be noticed that there is nothing to indicate any change in the interval as we pass from the longer to the shorter waves.

TABLE 40.—*Series in the fluorescence spectrum of uranyl nitrate hexahydrate* $[UO_2(NO_3)_2+6H_2O]$.

	Intensity.[1]	Reliability.[2]	$\frac{1^3}{\lambda}$	$\frac{1}{\Delta\lambda}$		Intensity.[1]	Reliability.[2]	$\frac{1^3}{\lambda}$	$\frac{1}{\Delta\lambda}$
A	v. d.	2	F 1760.1	.....	F	m.	1?	F 1631.3	.....
	v. d.	1	1846.0	85.9		d.	3	1718.4	87.1
	d.	2	1930.1	84.1		m.	4	1803.6	85.2
	m.	4	F 2018.2	88.1		m.	5	1889.6	86.0
						m.	5	1976.4	86.8
B	v. d.	3	F 1689.5	.....		d.	4	F 2061.9	85.5
	d.	3	1775.0	85.5					
	m.	4	1861.1	86.1		m.	4	A 2061.7	.....
	m.	5	1947.1	86.0		m.	4	A 2148.7	87.0
	str.	5	F 2034.5	87.4		m.	4	A 2234.1	85.4
	d.	3	A 2207.3	86.4×2		str.	3	A 2321.0	86.9
						v. d.	1	A 2491.9	85.5×2
C	d.	3	F 1699.0	.....	G	d.	3	F 1810.4	.....
	d.	2	1785.1	86.1		d.	4	1897.3	86.9
	d.	2	1869.0	83.9		v. d.	2	1983.1	85.8
	v. d.	1	1956.2	87.2		d.	1	A 2241.6	86.2×3
	m.	2	2041.5	85.3					
D	v. d.	1	F 1534.9	.....	H	v. d.	3	F 1649.7	.....
	d.	3	1621.0	86.1		v. d.	2	1737.4	87.7
	m.	4	1706.8	85.8		d.	1	1822.0	84.6
	str.	5	1792.5	85.7		m.	4	1906.7	84.7
	str.	5	1877.8	85.3		m.	4	1993.4	86.7
	str.	5	1963.6	85.8					
	d.	3	2050.0	86.4	I	v. d.	2	1826.0	.....
						v. d.	2	1911.7	85.7
E	v. d.	1	F 1540.1	.....					
	d.	2	1629.2	89.1	J	d.	3	F 1665.5	.....
	m.	3	1715.0	85.8		m.	3	1751.8	86.3
	str.	5	1800.0	85.0		d.	3	1837.8	86.0
	str.	5	1886.1	86.1		m.	4	F 1923.1	85.3
	str.	5	1972.5	86.4					
	str.	5	F 2058.5	86.0		d.	4	A 2268.3	86.3×4
						d.	1	A 2440.2	86.0×2
	m.	5	A 2058.6	.....					

[1] Estimated. Str., strong; m., medium; d., dim; v. d., very dim.

[2] The most reliable results (as indicated by the number and consistency of the individual measurements, the appearance of the negatives, etc.) are marked 5; the least reliable by 1.

[3] The unit in which $1/\lambda$ is expressed is such that for λ=5,000 Å. U. $1/\lambda$ is written 2,000.

In a spectrum consisting of so many bands, the occasional repetition of any given interval between bands is to be expected, even if the bands are distributed at random. It is proper to inquire, therefore, whether this interval of about 86.0 really occurs more frequently than would be expected for a random distribution. Data bearing on this point are plotted in the upper curve of figure 77. In this curve horizontal distances indicate the lengths of different possible intervals between

bands, while ordinates give the number of times each interval occurred. The range of possible error in the location of each band is arbitrarily assumed to be 2 units. Thus for a frequency interval 32 (abscissa) the ordinate is 10. This means that 10 pairs of bands were found for which the interval lay between 31 and 33.

It is evident from the chart that certain intervals occur with much greater frequency than would be expected if the bands were distributed at random, and this is most conspicuously true of the interval 86. It will be noted that the curve also shows lesser maxima for several other frequency intervals: e. g., 8, 16, 70, 78, and 94. These intervals correspond to the spacing of the bands in the successive groups which make up the spectrum.

On account of the fact that large, clear crystals could be obtained, the hexahydrate offered an especially favorable case for the study of the absorption spectrum. Observations were made with a number of different crystals ranging in thickness from a few tenths of a millimeter to 3 or 4 mm. The averages given in table 41 are in many cases based upon 15 or more independent measurements. In the case of the band at 2,148.7, for example, 17 measurements of wave-length were made, of which 3 were discarded because of the unsatisfactory character of the negatives. In the 14 measurements used in forming the average, the reciprocal wave-length ranged from 2,147.8 to 2,149.6, most of the values lying close to the average. In other cases the wave-length is much more uncertain. The extremely faint band at 2,536.4, for example, was observed on only two negatives, while the dim, broad band at 2,720.3 was observed only once. The reliability of the recorded average has been estimated in each case and is indicated in the table.

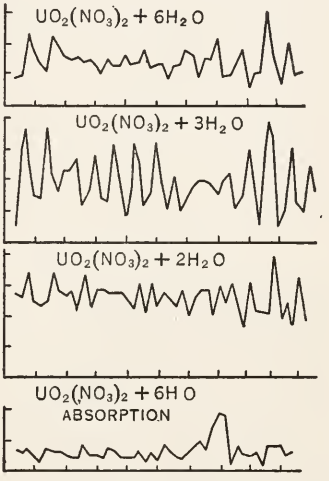

FIG. 77.—Frequency of occurrence of different intervals between bands. Abscissæ show the intervals (1 division=10); ordinates show the number of times the interval occurs (1 division =10).

A study of the absorption spectrum shows that an interval of about 71 between bands is of relatively frequent occurrence. (See the lower curve, fig. 77.) In several instances definite series exist with this constant interval. The values of $1/\lambda$ for the bands forming these series are given in table 41.

The two series *e* and *f* begin with reversible bands. Thus, the first band of series *e*, at $1/\lambda = 2{,}058.6$, can not be distinguished in position from the last band, $1/\lambda = 2{,}058.5$, of the fluorescence series E, while the first band, $1/\lambda = 2{,}061.9$, of series *f* is coincident with the band 2,061.7 of

TABLE 41.—*Series in the absorption spectrum of uranyl nitrate hexahydrate* $[UO_2(NO_3)_2+6H_2O]$.

Series.	Intensity.	Reliability.	$\frac{1}{\lambda}$	$\frac{1}{\Delta\lambda}$	Series.	Intensity.	Reliability.	$\frac{1}{\lambda}$	$\frac{1}{\Delta\lambda}$
	v. d.	2	2127.2	.....		m.	5	2148.7	.....
c	str.	4	2200.4	73.2		str.	5	2219.2	70.5
	d.	5	2272.3	71.9	h	str.	4	2290.2	71.0
			[2053.4]			m.	4	2359.4	69.2
	v. d.	4	2125.0	71.6		m.	4	2430.1	70.7
	d.	2	2196.8	71.8		d.	4	2500.0	69.9
	d.	4	2268.3	71.5					
d'	str.	3	2340.4	72.1	α	d.	5	2164.0	.....
	m.	3	2412.0	71.6		d.	4	2235.4	71.4
	str.	3	2484.1	72.1					
	str.	3	2555.3	71.2	β	str.	4	2321.0	.....
						m.	3	2390.0	69.0
	str.	5	[2058.5]	.....					
	m.	5	2058.6	.....	γ	str.	2	2464.3	.....
e	str.	4	2131.2	72.6		str.	4	2533.2	68.9
	m.	4	2203.8	72.6					
	d.	4	2277.8	74.0	δ	str.	4	2552.8	.....
						str.	4	2623.3	70.5
	d.	4	[2061.9]	.....		d.	2	2695.0	71.7
	m.	4	2061.7	.....					
f	str.	5	2134.1	72.4	δ'	d.	3	2559.5	.....
	m.	4	2207.3	73.2		m.	4	2630.5	71.0

fluorescence series F. There is some indication that several other absorption series may be looked upon as associated with fluorescence series in the same way. Thus the series α may perhaps be associated with a very weak fluorescence series falling between D and E. Two bands of such a series were occasionally observed at 1,968.0, and 2,053.4 (interval 85.4). The interval between the line at 2,053.4 and the first line of series α is 70.6, which is almost exactly the average interval for the absorption series. Again, in the case of series h we might expect an absorption band to fall at 2,078.7, while series H might have a fluorescence band at nearly the same point, viz, 2,079.3. Neither band was observed; but it must be remembered that the detection of reversible bands is only possible when the conditions of excitation are suitable. Any trace of fluorescence tends to mask an absorption band, and vice versa. The scarcity of bands, either of fluorescence or absorption, in the "reversal region" lying between 2,060 and 2,120 is perhaps due to this cause. There are other cases which suggest the same relationship between fluorescence and absorption series, although less definitely.

While there are thus strong reasons for believing that certain fluorescence series are to be looked upon as associated, in the manner indicated above, with absorption series, yet there are several series in the fluorescence spectrum for which no related absorption series have been observed; and, on the other hand, there are several absorption series which do not appear to be related with the observed fluorescence. In

this respect the systematic relation of fluorescence and absorption is not so completely brought out as in the spectra of the chlorides.

The observed intervals between bands are not so nearly constant in the case of the absorption series as in the fluorescence series. It seems to us probable that this is due to the greater uncertainty in the wave-length determinations; for on account of the lack of sharpness of the absorption bands and their greater width, as compared with fluorescence bands, the accuracy that is attainable in determining their location is considerably less than in the fluorescence spectrum.

It will be noted also that the interval between bands is different for different series. For series e the average interval is 73.1; for series d' it is 71.7; for series h, 70.3; while for the two pairs of lines in the ultra-violet, which have been designated as series β and γ, the interval is in one case 69.0 and in the other 68.9. This change in interval as we pass from one series to another, which is too great to be accounted for by experimental errors, appears of especial significance when it is remembered that in the fluorescence spectrum the interval is the same for all the series.

One of the most puzzling points brought out by the detailed study of the observed spectra is the fact that a considerable number of the absorption bands are spaced with the interval corresponding to the fluorescence series, and in some cases appear to form a continuation of these series. In such cases the reciprocal wave-lengths for these bands are included in table 40, but are preceded by the letter A. Thus, there are four absorption bands, in addition to the reversible band, which apparently belong to series F. If it is assumed that they do form a part of this series, the average interval for the whole series comes out exactly the same as for the fluorescence bands alone. Series J appears to include two absorption bands, and series B, E, and G each show one band. On the whole, however, we are inclined to look upon these cases as the result of accidental coincidences and to believe that the fluorescence series do not extend into the absorption region beyond the reversible band.

The interval of about 70, which appears to be characteristic of the absorption spectrum, is also found in the fluorescence spectrum. Thus the bands of series C are displaced from those of series E by intervals ranging from 69.0 to 70.2. A similar relation appears to exist between series J and series H, the average displacement being 70.1. Between series B and A the average shift is 70.6, between series F and H, 68.1, between series D and B, 69.1. With the exception of series I the series thus seem to be grouped in pairs, the interval between pairs being in the neighborhood of 70. It seems not unlikely that a companion series exists for I also, since faint bands were occasionally observed at 1,826.0 and 1,911.7 (interval 85.7) which are displaced by the intervals 71.3 and 71.4 from the corresponding bands of series I.

The Trihydrate: $UO_2(NO_3)_2+3H_2O$.

The trihydrate crystallizes in the triclinic system with the axial ratios $a : b : c = 1.2542 : 1 : 0.70053$.[1] The crystals were grown by evaporating the nitric-acid solution in a desiccator over caustic potash and sulphuric acid or over calcium chloride. To obtain large crystal plates the bottom of a dish 6 cm. in diameter was covered with the solution to a depth of about 2 mm. and the solution was "seeded" near the center. A cover was then placed over the solution with a small opening at the center, so that evaporation took place directly over the crystal. The trihydrate was also obtained in the form of a fine powder by efflorescence of the hexahydrate crystals in dry air. Although most of the observations recorded below were made with single crystals, a few measurements were made, with concordant results, on the powder. In the fluorescence spectrum visual observations only were made. In the absorption spectrum the measurements were in most cases photographic.

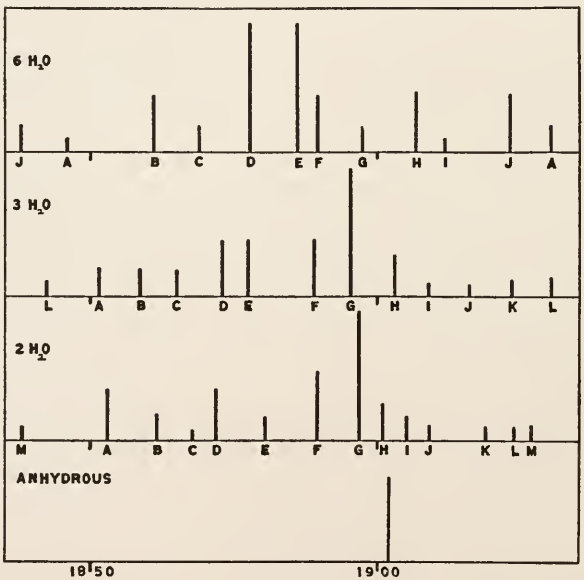

Fig. 78.—One group of bands from the fluorescence spectrum of each of the salts studied. The spectrum of the hexahydrate contains 7 such groups; that of the trihydrate, 6; the dihydrate, 5; and the anhydrous salt, 3.

The fluorescence spectrum of the trihydrate was found to consist of 63 bands, of which 55 fell into 12 constant-interval series of from 3 to 6 bands each. The intervals for the different series ranged from 86.5 to 87.5, the average being 86.8. The reciprocal wave-lengths are given in table 42. The numbers in parentheses refer to absorption bands which seem to fall into the fluorescence series. The relative intensities

[1] Wyrouboff. Sur quelques composés de l'uranium, Bull. Soc. Française Mineral, 32, 349–350. 1909.

of the bands are shown roughly in figure 78, where a typical group, *i. e.*, one band from each series, has been plotted for each of the salts studied.

TABLE 42.—*Series in the fluorescence spectrum of uranyl nitrate trihydrate,* $UO_2(NO_3)_2+3H_2O$.

A. 1677.0, 1765.0, 1851.5, 1938.8, 2025.0, (2112.7, 2200.2).
B. 1686.1, 1772.0, 1858.7, 1945.7, 2033.2, (2120.7).
C. 1778.7, 1865.1, 1952.9, 2041.1, (2041.1).
D. 1699.8, 1785.9, 1873.0, 1959.1, 2046.8, (2134.0, 2220.6, 2307.9).
E. 1704.2, 1791.8, 1877.4, 1965.3, 2051.0.
F. 1629.2, 1715.2, 1802.1, 1889.0, 1976.4, 2064.3?
G. 1637.2, 1722.8, 1808.7, 1895.3, 1982.3, 2070.7.
H. 1643.9, 1729.2, 1816.1, 1903.0, 1989.9, 2076.3, (2076.5, 2251.2).
I. 1821.3, 1908.9, 1995.9, (2083.8).
J. 1741.8, 1828.2, 1915.9, 2002.1, (2089.7).
K. 1748.6, 1835.3, 1923.3, 2009.8.
L. 1667.2, 1755.0, 1842.4, 1930.1, 2017.4, (2103.5, 2189.2, 2277.9).

The second curve of figure 77, which shows the frequency of occurrence of the different possible intervals between the bands of the fluorescence spectrum, indicates a remarkably regular grouping of the bands. Besides the principal interval 87 which is characteristic of the series in this spectrum, a number of other intervals are almost equally prominent, *e. g.*, 7, 14, 30, 36, 43.5, 50, 80, 94. In the case of each of these intervals the frequency of occurrence is far above the average. These intervals, of course, correspond to the spacing of the bands in the groups. Thus the interval 43.5, which is just half the principal interval 87.0, occurs twice in each group, the bands of series K lying half-way between the bands of series F and the bands of series L half-way between those of series G. In each case the two series might be combined to form a single series with half the interval. Since, however, the bands of the combined series would be alternately strong and weak, it does not appear that such a combination is justified.

In the absorption spectrum of the trihydrate, 48 bands were observed, several of which, however, were so faint and indistinct as to make their existence doubtful. As in the case of the hexahydrate, an interval between bands of a little more than 70 is of frequent occurrence, and 37 of the bands (including all that are strong and well defined) can be arranged in 9 constant-interval series. The interval does not appear to be the same for all of these series, however. In one case the interval is as high as 73.8, while in another case its value is 71.0. For most of the series the interval lies near 72.0.

In many instances the absorption series start with reversed fluorescence bands. Reversals are especially sharp and definite in the case of the final bands of series C, G, H, and I ($1/\lambda$=2,041.1, 2,070.7, 2,076.3, 2,104.9). In other cases, the absorption series begins at a point where a fluorescence band might be expected, but where none was actually observed. Thus, we should expect the final bands of series I, J, and K to lie at 2,082.7, 2,009.0, and 2,096.6 respectively. These bands were not observed, probably because of the fact that the three series in question

are made up of very faint lines. But the first bands of the absorption series *i*, *j*, and *k* fall at 2,083.8, 2,089.7, and 2,095.6, and it would seem, therefore, that they might properly be looked upon as resulting from the reversal of the final bands of the corresponding fluorescence series, even though these bands escaped observation.

The reciprocal wave-lengths for the principal absorption series are given in table 43. Each series is lettered in such a way as to indicate

TABLE 43.—*Series in the absorption spectrum of uranyl nitrate trihydrate* [$UO_2(NO_3)_2+3H_2O$].

b	*B* = 2033.2	*b* =(2033.2)	2107.0	2180.8.		
c	C = 2041.1	*c* = 2041.1	2112.7	2186.7.		
c'	*C'*=?	*c'*= 2043.3	2116.0	2189.7	2261.0.	
f'	F'= 2058.5	*f'*= 2057.6	2129.0	2200.2	2271.7.	
g	G = 2070.7	*g* = 2071.7	2142.7	2213.2	2285.7	2357.9.
h	H = 2076.3	*h* = 2076.5	2148.6	2220.6	.....	2368.0.
i	I =(2082.7)	*i* = 2083.8	2154.5	2226.9	2297.8	2368.0.
j	J =(2090.0)	*j* = 2089.7	2162.0	2235.4	2307.9.	
k	K =(2096.6)	*k* = 2095.6	2166.7.			
l'	L'=?	*l'*= 2103.0	2173.4	2245.7	2317.5	

the fluorescence series with which it appears to be related, *e. g.*, the first band of series *c* is the reversal of the last band of series C. In each case also the reciprocal wave-length is given for the last band of the fluorescence series. The numbers in parentheses indicate bands that were not observed, but would be expected to occur with the indicated value of $1/\lambda$.

It is to be observed that no absorption series were found which corresponded to the fluorescence series A, D, E, and L. On the other hand, no fluorescence series were observed to correspond with the absorption series *c'* and *l'*.

THE DIHYDRATE: $UO_2(NO_3)_2+2H_2O$.

Although the dihydrate has been made by several observers, the crystalline form does not appear to have been studied. The crystals used in this investigation were in most cases made by heating a tube containing the crystallized trihydrate to a temperature somewhat above 100° C. and passing through it a current of air which had been run through a mixture of sulphuric acid and nitric acid and over phosphorus pentoxide. The melted trihydrate slowly evaporated and recrystallized as dihydrate without losing nitric acid. The tube was then sealed up to prevent the entrance of moisture. The dihydrate was also prepared synthetically by treating dry H_2UO_4 with the "monohydrate" nitric acid, the two being sealed in a glass tube and allowed to react. The crystals obtained were in each case small, so that the observations were made on a mass of crystals having no systematic arrangement of the axes.

Seventy-four bands were observed in the fluorescence spectrum, 61 of which fell into 12 constant-interval series of from 4 to 6 bands each. The interval ranged from 87.6 in series F to 88.3 in series A, but in most cases lay near the average of all, viz, 88.1.[1] The values of $1/\lambda$

[1] For series C, which contained two bands only, the interval was 87.2.

are given in table 44, and a typical group, consisting of one band from each series, is shown in figure 78. Many of the bands that do not fall into these 12 series nevertheless seem to belong to similar series of which only 2 or 3 bands could be detected. Two of these suspected series have been included in figure 78, where they are indicated by dotted lines.

TABLE 44.—*Series in the fluorescence spectrum of uranyl nitrate dihydrate* [$UO_2(NO_3)_2+2H_2O$].

A.	1676.7	1765.9	1853.0	1942.7	2030.7		
B.	1684.9	1773.7	1861.6	1951.0	2037.9		
C.	1780.6	1867.8					
D.	1609.0	1695.5	1783.5	1871.8	1959.7	2047.4	
E.	1618.9	1705.9	1794.4	1880.3	1967.5		
F.	1625.3	1714.3	1801.5	1889.5	1977.1	2063.1	
G.	1632.7	1721.2	1808.5	1896.8	1985.2	2072.5	(2072.7)
H.	1637.7	1725.3	1814.6	1900.8	1989.7	2077.3	(2078.2)
I.	1641.5	1729.8	.....	1905.1	1993.8		
J.	1645.3	1734.6	1821.2	1909.0	1998.4		
K.	1830.5	1918.3.					
L.	1658.4	1745.5	1834.9	1923.8	2009.3	(2095.9)	
M.	1751.0	1838.2	1926.8	2015.5	(2102.7	2191.3	2278.0)

The absorption bands were located by observing the spectrum of light from a continuous source after diffuse reflection from a mass of small crystals. Although the bands observed in this way are surprisingly sharp, the method is not so satisfactory as that in which the light is analyzed after direct transmission through a single crystal. It is doubtful whether the reflection method gives as great accuracy in the location of the bands, and many of the weaker bands, which would have been easily detected if large crystals had been available, were probably not observed at all. For this reason, perhaps, the absorption spectrum of the dihydrate shows only four well-defined series. The reciprocal wave-lengths for these series are given in table 45. The interval between bands is 70.0 for series *m*, 70.4 for series *j*, and 71.3 for series *g* and *h*. In each case the first band in the absorption series occupies nearly the same position as the last band in one of the fluorescence series.

TABLE 45.—*Series in the absorption spectrum of uranyl nitrate dihydrate* [$UO_2(NO_3)_2+2H_2O$].

G=	2072.4	*g*= 2072.7	2144.7	2215.3.		
H=	2077.3	*h*= 2078.2	2149.4	2218.9	2290.4	2362.9
J=(2085.7)		*j*=(2086.1)	2156.6	2227.2	2297.3.	
M=(2103.6)		*m*= 2102.7	2172.7	2242.7.		

THE ANHYDROUS NITRATE.

Specimens of uranyl nitrate that were in all likelihood anhydrous, and which certainly contained less water than the dihydrate, were prepared by allowing nitric anhydride, N_2O_2, to react with uranic oxide. The nitric anhydride was distilled from a mixture of nitric acid and phosphorus pentoxide, while the uranic oxide was prepared by heating uranic acid, H_2UO_4. In preparing the oxide, the heating was not continued so long as to completely drive off the water from the uranic

acid, since when this was done no reaction occurred between the oxide and the nitric anhydride.

At temperatures above 30° C. the N_2O_2 reacts with the mixture of UO_3 and H_2UO_4 to form uranyl nitrate, presumably anhydrous, and a considerable amount of HNO_3. To free the specimen from acid, the tube containing it was placed in a freezing mixture until the N_2O_5 was frozen, when the HNO_3, which still remained a liquid, was poured off. This process was repeated several times. While the amount of water remaining after this treatment must have been extremely small, we cannot feel certain that all traces were removed, and it is possible, therefore, that the nitrate formed may have consisted in part of the monohydrate. No fluorescence bands belonging to the other hydrates could be observed. The method of preparation was varied by changing the temperature at which the reaction was allowed to occur, and by heating the salt, after it had been formed, to different temperatures and for different periods.

The fluorescence spectra of the different preparations differed widely. In one case the spectrum was found to consist of 3 narrow bands only, but in all other cases bands were observed which remained broad (about 100 Å. U.) even at the temperature of liquid air. These bands were spaced with a constant-frequency interval of approximately 88 to 89. It seems probable that these broad bands were due to the solution of the anhydrous salt in nitric acid. To test this point a specimen was prepared under conditions which made certain the presence of a considerable excess of nitric acid. The fluorescence spectrum contained two series of broad bands, the central band of the stronger series lying at $1/\lambda = 1{,}939.0$ and that of a weaker series at $1/\lambda = 1{,}920.0$. The specimen was then gently heated and the nitric acid driven off was condensed in a connecting-tube. After this process had continued for a short time, several series of narrow bands or lines appeared in the fluorescence spectrum (at $-186°$ C). As this procedure was repeated, the line spectrum became more prominent and the broad bands fainter. In one instance the specimen was heated nearly to decomposition—in fact, part of the salt was undoubtedly decomposed—and in this case the very faint fluorescence spectrum consisted of three narrow bands only. The same three bands were observed in the case of most of the specimens that were prepared in the attempt to remove the water of crystallization, although in other cases they were accompanied by other lines or broad bands. It seems probable that these three bands constitute the brightest part of the fluorescence spectrum of the anhydrous salt, and that the additional lines and bands that were observed in some specimens are due to traces of the monohydrate or to a solution of the nitrate in HNO_3. The three bands formed a series with the interval 88.5, the central band lying at $1/\lambda = 1{,}902.0$.

Summary of Section I.

(1) In the case of each of the nitrates, the fluorescence spectrum is made up of series in which the intervals between bands are constant and the same for all of the series. The interval increases slightly, but unmistakably, as the amount of water of crystallization decreases. For the hexahydrate the interval is 86.0, for the trihydrate 86.8, for the dihydrate 88.1, and for the anhydrous salt 88.5.

(2) Numerous constant-interval series occur in the absorption spectrum, the interval being approximately 71. But the interval does not appear to be the same for different series, even when these occur in the spectrum of the same salt. No systematic variation with the amount of water of crystallization could be detected.

(3) Nearly all of the series in the absorption spectrum have their origin in the "reversing region," the first member of the absorption series being in coincidence with the last member of a fluorescence series and constituting a "reversible" band.

(4) There is some slight resemblance between the different hydrates as regards the grouping of the bands (see fig. 77). In each case, for example, a certain short interval appears with a frequency considerably above the average. In the case of the hexahydrate and the dihydrate this interval is about 8; in the case of the trihydrate is almost exactly 7. The interval 14, in the case of the trihydrate, and 16, in the case of the other two salts, is also of unusually frequent occurrence.

(5) It is clear from inspection of figure 78, in which a characteristic group of bands is shown for each of the hydrates studied, that the different spectra are not in the least similar in their general appearance. It might at first appear that the three hydrates have one series in common, viz, that designated as series F. But while the central band of this series does occupy practically the same position in each of the three spectra, the fact that the interval between bands is different for the different salts causes the bands to fall more and more out of step as we proceed in either direction from the center of the spectrum.

On the whole, the spectra of the different hydrates differ from one another fully as much as do the spectra of two different uranyl salts. This result is surprising, since it is customary to think of water of crystallization as rather loosely attached and therefore incapable of exerting a great influence upon properties which depend upon the internal structure of the molecule. Indeed, were the amount of water of crystallization the only difference between the forms of uranyl nitrate under consideration, we should look upon the attachment as more intimate than has generally been supposed.

There is, however, another distinction, that of crystalline structure, and, as will appear from the subsequent sections of this chapter, the crystal form has a profound influence upon the character of the fluorescence and absorption spectra of the uranyl salts.

II. THE DOUBLE NITRATES: INFLUENCE OF CRYSTAL FORM.[1]

There is good reason to think that crystal form has an important bearing upon the structure and arrangement of fluorescence spectra. The polarized spectra of the four double uranyl chlorides, described in Chapter VI, are almost identical in arrangement and in the absolute position, relative intensity, and resolution of their bands. These substances all crystallize in the triclinic system. Further evidence bearing upon this subject will be found in section III of this chapter.

Our object in the present section is to describe the fluorescence and absorption of four double uranyl nitrates and to throw further light on the rôle played by crystal structure.

The two pairs of double nitrates studied are mono-ammonium uranyl nitrate, $NH_4UO_2(NO_3)_3$; di-ammonium uranyl nitrate, $(NH_4)_2UO_2(NO_3)_4$ $2H_2O$; the mono-potassium uranyl nitrate, $KUO_2(NO_3)_3$; and the di-potassium uranyl nitrate, $K_2UO_2(NO_3)_4$.

The crystallographic features of these four compounds may be briefly specified as follows:

(1) *The mono-ammonium salt*, which crystallizes from a solution of the two component salts in concentrated nitric acid, was described by Meyer and Wendel[2] and crystallographically by Steinmetz.[3] The crystals are of the trigonal system, with an axial ratio of $a : c = 1 : 1.0027$.

(2) *The di-ammonium salt* crystallizes from a slightly acid water solution of the two salts in which the ammonium nitrate is in excess of that required for the mono-ammonium salt. This salt was at first thought to be the α modification of ammonium uranyl nitrate made by Rimbach[4] and measured by Sachs,[5] but an examination of the spectrum of the α modification so-called proved that it was simply uranyl nitrate hexahydrate. The crystals analyzed by Rimbach were probably the mono-ammonium form, as this sometimes forms in the same solution. The crystals of the di-ammonium salt belong to the monoclinic system.

(3) *The mono-potassium salt* crystallizes from nitric-acid solution in the rhombic system, as described by Steinmetz, with axial ratio $a : b : c = 0.8541 : 1 : 0.6792$.

(4) *The di-potassium salt* crystallizes with reluctance; but when seeded from an acid aqueous solution, it forms in beautiful, fluorescent crystals of the monoclinic system. The axial angle is $\beta = 90° \pm$ and the axial ratio $a : b : c = 0.6394 : 1 : 0.6190$. The composition is different from that of the di-ammonium salt, since it lacks the water of crystallization.

Both visual and photographic measurements of the spectra were taken, and, since they agreed well, were averaged together. When

[1] Howes, H. L., and D. T. Wilber: Physical Review (2), IX, p. 125 (1917).
[2] Meyer and Wendel, Ber. d. d. Ch. Ges., vol. 36, 4055. 1903.
[3] Steinmetz, Groth's Chem. Krys., II, p. 150.
[4] Rimbach, Ber. d. d. Ch. Ges., vol. 37, 472. 1904.
[5] Sachs, Zeitschr. f. Krys., vol. 38, 497. 1904.

possible the absorption spectrum was obtained by transmitted light. The crystals from an acid solution were of a deeper green color than those from a water solution, which necessitated grinding to about 0.4 mm. thickness to make them sufficiently transparent. Since the immersion in liquid air spoiled a crystal, many crystals of each form had to be prepared.

Since, as is usual with the uranyl salts, we have in these spectra series of constant-frequency intervals, the location of the bands (tables 46, 47, 48, 49) is indicated in frequency units. As elsewhere in this treatise, fluorescence series are denoted by capital letters (A, B, C, etc.) and the related absorption series by *a*, *b*, *c*, etc., or where the relation is not obvious, by Greek letters.

The four spectra are mapped in the usual manner in figure 79.

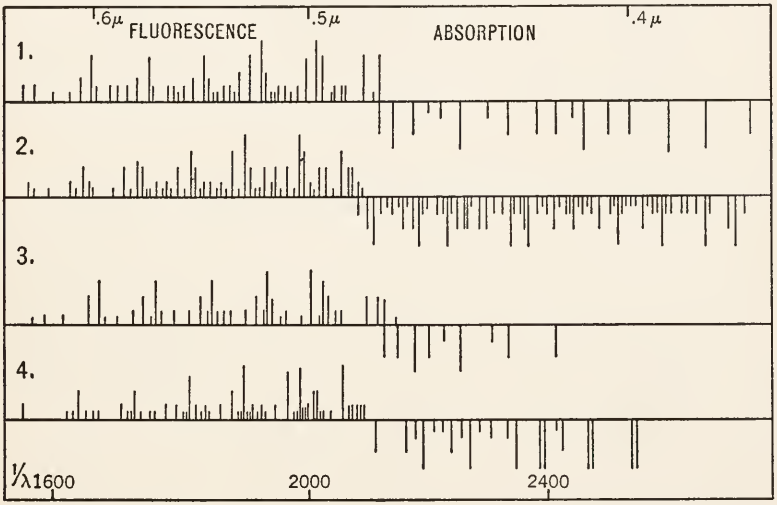

FIG. 79.—1. Fluorescence and absorption spectra of mono-ammonium uranyl nitrate, $NH_4UO(NO_3)_3$. 2. Diammonium uranyl nitrate, $(NH_4)_2UO_2(NO_3)_4.2H_2O$. 3. Mono-potassium uranyl nitrate, $KUO_2(NO_3)_3$. 4. Di-potassium uranyl nitrate, $K_2UO_2(NO_3)_4$.

In the spectra of these double nitrates, the relation of absorption to fluorescence is somewhat simpler than is the case with the uranyl nitrates described in section 1 of this chapter, but it is less systematic and complete than in the spectra of the double chlorides. Thus, in *mono-ammonium* and *mono-potassium* salts (table 46 and 48), there are not sufficient absorption series to match all the fluorescence series, but there are no absorption series that do not join. In the *di-ammonium* spectrum (table 47) there is a related absorption series for each fluorescence series and three extra absorption series that are not obviously related to fluorescence. (See plate 1, *b*.) In the spectrum of the *di-potassium salt*, fluorescence series B, D, G, I, and J have no corresponding absorption of measurable intensity, while there are two absorption series, *l'* and *g*, apparently with a direct reversing linkage with the fluorescence. As to the completeness of classification of bands, it can

be said that not a fluorescence or absorption band of any of the salts fails to fit into one of the constant-frequency series.

TABLE 46.—*Series in the fluorescence spectrum of mono-ammonium uranyl nitrate.*

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
A	1797.6	88.3	G	1573.9	89.1	K	1859.1	89.7
	1885.9	86.2		1663.0	88.0		1948.8	87.0
	1972.1	86.2		1751.0	87.2		2035.8	
	2058.3			1838.2	87.7			
B	1629.4	88.7		1925.9	87.9	L	1602.1	90.6
	1718.1	87.8		2013.8	87.5		1692.7	88.2
	1805.9	87.5		2101.3			1780.9	88.1
	1893.4	90.7	I	1670.0	88.0		1869.0	84.5?
	1984.1			1758.0	87.7		1953.5	87.5
D	1555.5	89.6		1845.7	88.5		2041.0	
	1645.1	88.9		1934.2	88.1	M	1704.2	86.2
	1734.0	87.0		2022.3	87.9		1790.4	88.4
	1821.0	88.1		2110.2			1878.8	86.1
	1909.1	87.8	J	1852.5	88.9		1964.9	85.7
	1996.9	89.2		1941.4			2050.6	
	2086.1							

Series in the absorption spectrum of mono-ammonium uranyl nitrate.

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
a	2132.8	74.3	d	2163.1	74.2	i	2111.0	76.7
	2207.1	73.4		2237.3	75.9		2187.7	74.9
	2280.5	75.8		2313.2	73.7		2412.5	74.8
	2356.3	73.8		2386.9			2562.1	
	2430.1	72.4	g	2469.1				
	2502.5			.....	76.4×2			
				2621.9	72.0			
				2693.9				

In section I it was shown that in the spectrum of the uranyl nitrate the intervals of the fluorescence series are the same for all series within the errors of observation; in the case of the absorption series, however, the interval is not the same for all series. In the double nitrates we find an unmistakable variation in the fluorescence intervals as well as in the absorption. In the mono-ammonium nitrate the interval varies from 86.4 for series M to 89.0 for series B. In the di-ammonium nitrate the interval varies from 83.7 for G to 85.0 for E. In the mono-potassium nitrate spectrum the interval varies between 86.4 for G and 87.9 for J. In the di-potassium nitrate the interval varies between 86.2 for E and 87.6 for J.

The variation of the interval in the absorption series is of the same order of magnitude; *e. g.*, an extreme variation of 1.4 in the mono-ammonium, 3.5 in the di-ammonium, 4.3 in the mono-potassium, and 4.4 in the di-potassium nitrate. In this connection it was thought to be of interest to compare the ratios of related fluorescence and absorp-

tion intervals. In table 50 these ratios are given. The ratios are nearly constant for the mono-ammonium and mono-potassium uranyl nitrates, but differ in the case of the other two salts.

TABLE 47.—*Series in the fluorescence spectrum of di-ammonium uranyl nitrate.*

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
A	1773.6		F	1637.7		J	1664.5	
		83.8			84.8			84.2
	1857.4			1722.5			1748.7	
		84.4			84.3			83.5
	1941.8			1806.8			1832.2	
		84.1			84.3			86.0
	2026.4			1891.1			1918.2	
					85.4			86.3
				1976.5			2002.5	
B	1695.6				85.4			82.1
		83.9		2061.9			2084.6	
	1779.5							
		84.9				K	1754.1	
	1864.4			1564.0				83.9
		84.9			86.0		1838.0	
	1949.3			1650.0				85.1
					83.3		1923.1	
C	1786.4			1733.3				84.9
		85.2			83.5		2008.0	
	1871.6		G	1816.8				
		83.6			84.0			
	1955.2			1900.8			1595.4	
		84.4			84.5			85.6
	2039.6			1985.3			1681.0	
					83.2			83.4
				2068.5		L	1764.4	
D	1628.8							83.5
		84.3					1847.9	
	1713.1			1572.9				83.3
		83.2			84.9		1931.2	
	1796.3			1657.8				84.7
		84.5			83.8		2015.9	
	1880.8			1741.6				
		84.4	I		82.9			
	1965.2			1824.5				
		85.0			84.0			
	2050.2			1908.5				
					84.7			
				1993.2				
					83.7			
				2076.9				

Series in the absorption spectrum of di-ammonium uranyl nitrate.

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
a	2114.8		*e*	2131.0		*k*	2092.9	
		70.6			70.0			71.0
	2185.4			2201.0			2163.9	
		69.3			67.8			69.3
	2254.7			2268.8			2233.2	
		69.1×4			69.6			70.8
	2531.0			2338.4			2304.0	
		69.3×2			69.9			69.8
	2669.5			2408.3			2373.8	
					69.1			69.8
				2477.4			2443.6	
b	2178.1				68.2			67.5
		70.6		2545.6			2511.1	
	2248.7				69.1×2			73.6
		72.6		2683.8			2584.7	
	2321.3							72.8
		71.3					2657.5	
	2392.6		*g*	2140.8				
					70.1			
				2210.9			2102.3	
	2124.5				68.2			71.6
		69.3×3		2279.1		*l*	2173.9	
c	2332.5							71.2
		68.8					2245.1	
	2401.3			2077.3				71.7
		70.9			70.9		2316.8	
	2472.2			2148.2				
					69.8			
				2218.0			2384.8	
	2344.9				73.0			69.4
		70.0	*i*	2291.0		*a*	2454.2	
	2414.9				67.5			69.1
		69.8		2358.5			2523.3	
d	2484.7				70.7			69.4
		68.1		2429.2			2592.7	
	2552.8				68.5			
		68.4		2497.7				
	2621.2				69.3		2422.3	
				2567.0				68.6
						δ	2490.9	
								68.8
				2154.2			2559.7	
					70.1			68.4
				2224.3			2628.1	
			j		70.6×2			
				2365.4				
					70.7			
				2436.1			2538.1	
					68.1	*γ*		68.1
				2504.2			2602.2	

TABLE 48.—*Series in the fluorescence spectrum of mono-potassium uranyl nitrate.*

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
B	1725.3		G	1589.8	85.0	K	1615.8	84.6
	1813.8	88.5		1674.8	87.2		1700.4?	89.8
	1900.4	86.6		1762.0	86.5		1790.2	87.3
	1988.1	87.7		1848.5	86.4		1877.5	87.0
D	1569.1			1934.9	86.5		1964.5	85.8
	1655.9	86.8		2021.4	86.4		2050.3	86.0
	1742.7	86.8		2107.8			2136.3	
	1830.2	87.5				I	1683.2	
	1916.3	86.1	J	1867.6			1769.4	86.2
	2003.8	87.5		1955.1	87.5		1856.9	87.5
	2090.5	86.7		2043.2	88.1		1943.7	86.8
F	1754.1						2030.5	86.8
	1842.3	88.2					2118.2	87.7
	1928.5	86.2						
	2015.7	87.2						

Series in the absorption spectrum of mono-potassium uranyl nitrate.

	i/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
d	2167.0		*i*	2117.7	71.9	*k*	2140.3	72.9
	2238.3	71.3		2189.6			2213.2	74.7
	2313.8	75.5					2287.9?	
	2386.1	72.3						

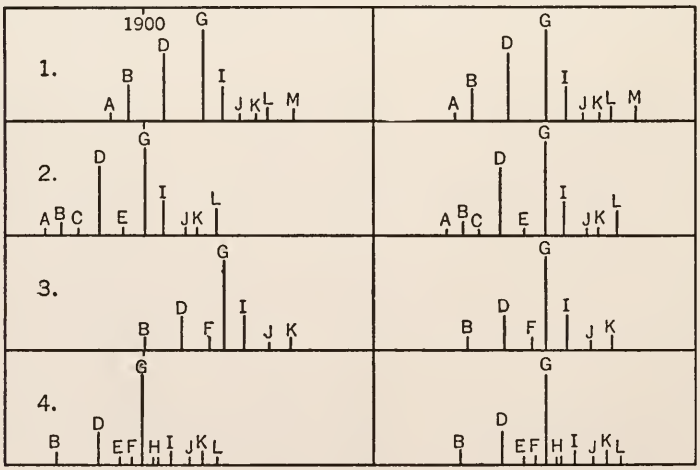

FIG. 80.—A single group from each of the four spectra.

1. Mono-potassium uranyl nitrate—trigonal. 2. Di-potassium uranyl nitrate—monoclinic. 3. Mono-ammonium uranyl nitrate—rhombic. 4. Di-ammonium uranyl nitrate—monoclinic. The bands occupy their natural positions in the left-hand panel, but have their strongest bands in vertical alignment in the right-hand panel.

That the crystal system to which a salt belongs is an important factor in determining the position of the bands can be seen in figure 80. In the left-hand panel a single group is shown in its natural position; in the right-hand panel the strongest bands of each group are placed in the same vertical line, to show the resemblance in grouping. This similarity is probably due to the fact that all four belong to the same chemical family. If we compare this grouping with that of the uranyl nitrate spectra in section I we find little resemblance, hence the grouping is probably characteristic of the double uranyl-nitrate family. In the left-hand panel it will be seen that the second and fourth groups occupy almost identical positions, while the first and third occupy positions which differ from one another and from the second or fourth. As has previously been stated, the second and fourth groups belong

TABLE 49.—*Series of the fluorescence spectrum of di-potassium uranyl nitrate.*

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
B	1775.2		F	1723.8?	84.8	I	1651.5	86.1
	1861.9	86.7		1808.6	85.5		1737.6	86.2
	1948.9	87.0		1894.1	86.2		1823.8	87.4
	2034.6	85.7		1980.3	88.5		1911.2	87.3
				2068.8			1998.5	87.0
D	1621.3		G	1554.0			2085.5	
	1708.0	87.7		1640.4	86.4	J	1831.8	
	1793.7	85.7		1727.6	87.2		1919.5	87.7
	1880.0	86.3		1813.2	85.6		2007.0	87.5
	1966.9	86.9		1899.0	85.8			
	2053.7	86.8		1986.2	87.2	K	1663.3	
E	1631.6		H	1903.7			1751.8	88.5
	1717.9	86.3		1906.8	86.5		1837.8	86.0
	1802.7	84.8		1989.7			1925.1	87.3
	1889.3	86.6		1993.8	86.6		2011.9	86.8
	1975.8	86.5		2075.8		L	1670.8	
	2062.2	86.4		2080.7			1757.8	87.0
							1844.6	86.8
							1931.4	86.8
							2018.3	86.9

Series in the absorption spectrum of di-potassium uranyl nitrate.

	1/λ	Δ(1/λ)		1/λ	Δ(1/λ)		1/λ	Δ(1/λ)
d	2196.6		*h*	2152.6		*l*	2105.9	
	2269.3	72.7		2224.3	71.7		2179.9	74.9
e	2210.9		*k*	2169.2		*l'*	2253.4	
	2285.7	74.8		2240.1	70.9		2325.1	71.7
f	2369.4			2310.9	70.8		2396.9	71.8
	2444.4	75.0		2382.6	71.7			
						δ	2361.6	
							2437.8	76.2
							2513.2	75.4

to the monoclinic crystal systems, the first to the trigonal and the third to the rhombic system. Since all four spectra vary slightly in their frequency intervals, the relative positions would change slightly if we compared homologous groups in the other end of the spectrum, but this gradual and slight shifting would not change the general condition, which indicates that the absolute position of a group is largely determined by the crystal system. This is not entirely new, as the four triclinic crystals of the double uranyl chlorides exhibit spectra which are as nearly coincident as could be expected of salts which vary in molecular weight.

TABLE 50.—*Average intervals.*

Mono-ammonium uranyl nitrate.										
Fluorescence series	A 86.6		D 88.3		G 87.7		I 88.1			
Absorption series	*a* 73.7		*d* 74.5		*g* 74.2		*i* 75.1			
Ratio of fluorescence to absorption	1.18		1.19		1.18		1.18			
Di-ammonium uranyl nitrate.										
Fluorescence series	A 84.4	B 84.4	C 84.3	D 84.5	E 85.0	G 83.7	I 83.9	J 83.8	K 84.8	L 84.0
Absorption series	*a* 69.2	*b* 71.6	*c* 69.8	*d* 68.9	*e* 68.7	*g* 68.8	*i* 69.6	*j* 69.7	*k* 70.9	*l* 71.5
Ratio of fluorescence to absorption	1.22	1.18	1.21	1.23	1.22	1.22	1.21	1.20	1.20	1.18
Mono-potassium uranyl nitrate.										
Fluorescence series	D 86.9		I 87.2		K 86.6					
Absorption series	*d* 73.2		*i* 71.9		*k* 74.1					
Ratio of fluorescence to absorption	1.18		1.16		1.17					
Di-potassium uranyl nitrate.										
Fluorescence series	D 86.6	E 86.2	F 87.2	H 86.5	K 86.9	L 86.9				
Absorption series	*d* 72.7	*e* 74.8	*f* 75.0	*h* 71.7	*k* 71.3	*l* 74.9				
Ratio of fluorescence to absorption	1.19	1.16	1.16	1.21	1.22	1.16				

Again, in the case of the uranyl nitrate, the crystals of the hexahydrate are of the rhombic system, while those of the trihydrate and dihydrate are of the triclinic system. In spite of slight shifts due to changing molecular weight, the strong bands of the two spectra produced by the crystals of the triclinic system agree fairly well, while the strong bands of the spectrum produced by the rhombic crystal reside in entirely different positions.

There is one more bit of evidence which adds weight to the above view. The chemical formulæ of the two potassium salts are more nearly alike than those of the two ammonium salts, since the diammonium salt has 2 molecules of water of crystallization, while the other salts have none, yet there is a greater difference between the first and second spectra than there is between the second and fourth spectra.

Summary of Section II.

(1) The spectra of the double uranyl nitrates resemble those of the previously studied uranyl salts in that the bands can be arranged in series having constant frequency intervals.

(2) These intervals, while constant for any given series, are different for different series.

(3) In the mono-ammonium uranyl nitrate and the mono-potassium uranyl nitrate the ratio of the interval of a fluorescence series to the interval of the absorption series which joins that fluorescence series is approximately a constant.

(4) Although the grouping of the bands shows a strong family resemblance in the four spectra, yet the absolute position of a group is largely determined by the crystal system.

III. RESOLUTION ON COOLING AND ITS DEPENDENCE ON CRYSTALLINE STRUCTURE.

The crystal system of any uranyl compound is an important factor in determining the character of its fluorescence and absorption spectra, as we have endeavored to show in the foregoing section. There is equally good evidence that *resolution* is dependent on the existence of a crystalline condition.

Table 51.—*Bands of fluorescence in canary glass.*[1]

At +20° C.		At −185° C.	
λ	$1/\lambda \times 10^3$.	λ	$1/\lambda \times 10^3$.
5280	1894	5330	1876
5180	1931	5140	1946

[1] R. C. Gibbs, Physical Review (1), vol. 30, p. 382.

Not all uranyl fluorescence spectra are well resolved on cooling. In the case of a piece of canary glass, for example, the rather unusually broad, vague doublet occurs at +20° (see table 51).

At the temperature of liquid air the doublet is partially resolved, but no narrow components appear.

The solid solution of uranyl phosphate in microcosmic salt, the phosphorescence of which has already been described in Chapter IV, yields a narrowing of the bands on cooling and a shift, but no resolution. (See table 52.)

TABLE 52.—*Bands of uranyl phosphate in microcosmic salt.*[1]

At +20° C.		At −185° C.	
λ	$1/\lambda \times 10^3$.	λ	$1/\lambda \times 10^3$.
5670	1764	5680	1761
5421	1845	5430	1842
5183	1929	5190	1927
4970	2012	4980	2008

[1] The bands are 160 Å. U. in width.

The inference that the failure to obtain resolution of the bands is due to the non-crystalline structure of the substance is confirmed by the observations described below.

EXPERIMENTS ON THE SPECTRA OF SODIUM URANYL PHOSPHATES.[1]

Stokes,[2] in an early paper on the ultra-violet spark spectra of the metals, described a fluorescent screen prepared by treating the ordinary uranyl phosphate with a solution of phosphoric acid and sodium or ammonium phosphate. While the uranyl phosphate is only feebly fluorescent, the double salts thus produced were very brilliant.

To investigate the fluorescence spectra of these double phosphates, the following preparations were made:

(1) A mixture of uranyl phosphate and sodium phosphate in the ratio of 4 molecular weights of $HUO_2PO_4.3\frac{1}{2}H_2O$ to 1 molecular weight of HUo_2PO_4.
(2) A similar mixture in proportions 2 to 1.
(3) A similar mixture in proportions 1 to 1.

These three specimens, when cooled to −180° C. and excited by radiation from the carbon arc, yielded precisely similar and well-resolved spectra. (See fig. 81, *1*, *2*, and *3*.)

In addition to the above, four further specimens were made by mixing increasing amounts of phosphoric acid with sodium uranyl phosphate, *i. e.*:

(4) One molecule of phosphoric acid to 2 molecules of uranyl phosphate and 1 molecule of sodium phosphate, giving the composition $H_3NaUO_2(PO_4)_2$ This was a powder, similar to preparations 1, 2, and 3.

[1] Howes and Wilber, Physical Review (2), VII, p. 394. 1916.
[2] Stokes, Philos. Trans., 152, p. 599. 1862.

(5) One molecule of phosphoric acid to 1 molecule of uranyl phosphate and 2 molecules of sodium phosphate. When dried, this contained much free sodium phosphate.

(6) Two molecules of phosphoric acid to 1 molecule of uranyl phosphate and 1 molecule of sodium phosphate. This specimen did not dry, but remained syrupy at room temperature and appeared to be vitreous at −180°.

(7) A solution of uranyl phosphate in a considerable excess of syrupy phosphoric acid. This gave a glass-like mass even at +20°.

The fluorescence spectra of these 7 substances are plotted to the usual frequency scale in figure 81.

Table 53 gives the location of the narrow bands, and approximately of the crests of the broad, unresolved groups; also the frequencies and frequency intervals.

It will be seen that the spectra of 1, 2, and 3 consist of recurring groups of narrow bands and that homologous members of these groups

TABLE 53.—*Wave-lengths and frequencies of the line series of the fluorescence of the sodium uranyl phosphates.*

	λ	1/λ	Δ1/λ		λ	1/λ	Δ1/λ
Series A.....	5640	1773.1		Series F.....	6015	1662.4	
(very dim)	5396	1853.1	80.0	(dim)	5739	1742.6	80.2
	5171	1933.8	80.7		5484	1823.4	80.8
					5248	1905.3	81.9
Average.....	.....	.....	80.4		5034	1986.3	81.0
Series B.....	6153	1625.2		Average.....	.....	.....	81.0
(dim)	5862	1705.8	80.6				
	5599	1785.9	80.1	Series G.....	5460	1831.6	
	5359	1865.9	80.0	(dim)	5227	1913.0	81.4
	5136	1947.0	81.1		5014	1994.6	81.6
Average.....	.....	.....	80.5	Average.....	.....	.....	81.5
Series C.....	6114	1635.7		Series H.....	5429	1841.8	
(very dim)	5827	1716.0	80.3	(very dim)	5199	1923.4	81.6
	5568	1796.0	80.0		4989	2004.6	81.2
	5327	1877.3	81.3				
Average.....	.....	.....	80.5	Average.....	.....	.....	81.4
Series D.....	6075	1646.0		*Series B'.....	6169	1621.0	
(medium)	5794	1726.0	80.0	(medium).....	5877	1701.5	80.5
	5538	1805.6	79.6		5607	1783.5	82.0
	5299	1887.1	81.5		5363	1864.6	81.1
					5136	1947.0	82.4
Average.....	.....	.....	80.4	Average.....	.....	.....	.....
Series E.....	6350	1574.9					
(very strong)	6040	1655.7	80.8				
	5760	1736.2	80.5				
	5506	1816.2	80.0				
	5270	1897.4	81.2				
	5057	1977.6	80.2				
Average.....	.....	.....	80.5				

* Series B' is found in spectrum No. 5 only.

TABLE 53.—*Wave-lengths and frequencies of the broad-band series of the fluorescence of the sodium uranyl phosphates.*

	λ	1/λ	Δ1/λ		λ	1/λ	Δ1/λ
Spectrum No. 4....	6219	1608.0	83.6	Spectrum No. 6....	5932	1685.8	86.0
	5909	1692.6	80.1		5644	1771.8	84.2
	5641	1772.7	82.6		5388	1856.0	86.9
	5390	1855.3	83.4		5147	1942.9	
	5158	1938.7	82.3				
	4948	2021.0		Average.....	.....	.....	85.3
Average.....	.....	.....	82.6	Spectrum No. 7....	5958	1678.4	88.1
Spectrum No. 5....	5927	1687.2	83.7		5661	1766.5	85.4
	5647	1770.9	81.6		5400	1851.9	87.2
	5398	1852.5	80.2		5157	1939.1	87.3
	5174	1932.7	85.1		4935	2026.4	
	4956	2017.8		Average.....	.....	.....	87.0
Average.....	.....	.....	82.7				

form the usual constant-interval series. The interval, which is *the same for all* within the errors of observation, is the shortest yet observed in the study of the fluorescence of the uranyl salts. Position as well as the arrangement of the bands is identical, and it is highly probable that we have to do with the same crystalline fluorescent compounds in these three preparations.

The broad bands of specimens 4 and 5 form series with a constant interval of 82.5 units. Evidently the increase in the proportion of phosphoric acid tends to suppress the strongest line series and merge the dimmer series into broad bands. With the increasing predominance of the broad bands, caused by the increasingly larger proportion of acid present, there is a simultaneous increase in interval from 82.5 units to 85.1 units for specimen No. 6, and 87.0 units for specimen No. 7.

Experiments similar to the above were made in which ammonium phosphate was substituted for sodium phosphate. The results were in all respects analogous to those above described.

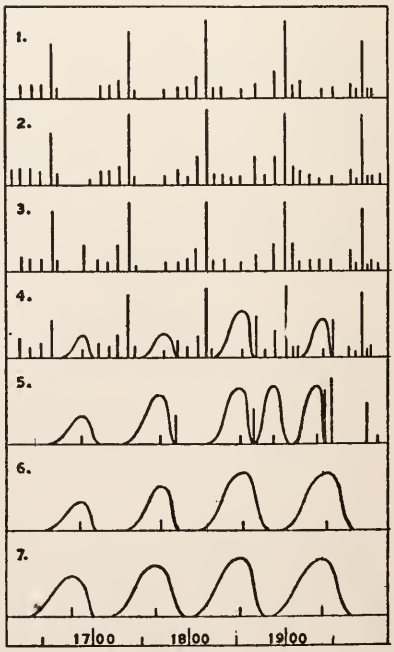

FIG. 81.

That in general the resolution of the uranyl spectra by cooling occurs only when the fluorescing substance is in crystalline form is further substantiated by numerous experiments on frozen solutions to be described in detail in Chapter X.

Summary of Section III.

(1) Where uranyl compounds occur in solid solution, as in canary glass, or in a bead of microcosmic salt, the banded fluorescence spectrum with constant frequency intervals, as observed at +20° C., is *not* further resolved into groups of narrow, line-like bands by cooling to the temperature of liquid air.

(2) Sodium uranyl phosphate or ammonium uranyl phosphate, when prepared in the form of crystalline powder, gives fluorescence spectra which are fully resolved at low temperatures.

(3) In the presence of an excess of phosphoric acid, where the above compounds, or uranyl phosphate, form solid solutions of vitreous structure, resolution does not occur on cooling.

(4) There is reason to think that the dependence of resolution by cooling upon the existence of crystalline structure applies in general to the fluorescence of the uranyl salts.

VIII. THE ACETATES.

The uranyl acetates afford a broader field for investigation than the chlorides or nitrates, the spectra of which have been considered in previous chapters.

In addition to two forms of the single acetate $UO_2(C_2H_3O_2)_2$, we have the double salts of all the alkali metals except cæsium; the double salts of calcium, barium, strontium, magnesium, zinc, lead, silver, and manganese; the triple salt $NaMg\ UO_2(C_2H_3O_2)_5$.

In the fluorescence spectra of the acetates, as in the case of all uranyl salts thus far studied, the broader bands observed at room temperature are resolved into groups when the substance is excited at the temperature of liquid air, and the constitution of these groups, which repeat themselves at regular intervals from the red to the region in the blue, where absorption begins to replace fluorescence, is very similar in the acetates to that of the groups in the spectra of the compounds already discussed.

THE SINGLE ACETATE.

Two distinct varieties of this salt were available for observation—the finely powdered anhydrous form, $UO_2(C_2H_3O_2)_2$, and the crystalline form, $UO_2(C_2H_3O_2)_2.H_2O$.

The spectra of the two are very similar in appearance; each being characterized by two strong, well-defined series forming a set of doublets. They are easily distinguished, however, by the widely different location of the doublets. In the spectrum of the anhydrous variety these occur near the group centers of the alkaline double salts, whereas in the crystalline form they fall nearly midway between these groups.

The strong series of the crystalline salt, which we have denoted as E and F, frequently appear in greatly reduced intensity in the spectra of the double salts, due doubtless to the presence of traces of the single acetate. The strong doublets C and D of the anhydrous acetate, if they ever appear in the spectra of the double salts, would be more difficult to detect, as they would overlap bands in the groups of the latter.

Wave-lengths and frequencies of these two forms of uranyl acetate are given in tables 54 and 55. Intensities are designated as *very strong* (vs), *strong* (s), *medium* (m), *dim* (d), *very dim* (vd), and *very very dim* (vvd).

Studies of a Single Group.

Since the acetates, like the chlorides and nitrates discussed in previous chapters, have spectra consisting of similar recurring groups, it is convenient and sufficient, in the study of the structure of the ensemble of the fluorescence, to consider a single group. For this

TABLE 54.—*Fluorescence bands in spectrum of uranyl acetate (anhydrous), −185°.*

Group.	Series.	μ	$1/\mu \times 10^3$	Int.	Group.	Series.	μ	$1/\mu \times 10^3$	Int.
3	C″	0.6037	1656.4	m.	6	A	0.5295	1888.5	d.
	D	.6011	1663.5	m.		B	.5273	1896.6	d.
	E	.5975	1673.6	vd.		C	.5229	1912.5	d.
	F	.5950	1680.6	vd.		C′	.5223	1914.4	s.
4	A	.5822	1717.5	d.		D	.5202	1922.4	s.
	B	.5799	1724.3	d.		E	.5183	1929.4	vd.
	C	.5749	1739.4	d.		F	.5161	1937.5	m.
	C′	.5739	1742.6	m.		G	.5117	1954.4	vd.
	D	.5713	1750.5	m.		H	.5088	1965.5	vd.
	E	.5687	1758.5	vd.	7	A	.5062	1975.4	vd.
	F	.5663	1765.7	vd.		B	.5041	1983.6	vd.
5	A	.5548	1802.6	d.		C′	.5006	1997.4	d.
	B	.5523	1810.5	d.		D	.4979	2008.6	s.
	C′	.5481	1824.6	d.		E	.4961	2015.6	vd.
	C	.5469	1828.5	s.		F	.4940	2034.3	d.
	D	.5445	1836.4	s.					
	E	.5424	1843.6	d.					
	F	.5401	1851.5	d.					
	G	.5352	1868.5	vd.					
	H	.5318	1880.5	vd.					

TABLE 55.—*Fluorescence bands in spectrum of uranyl acetate* $[UO_2(C_2H_3O_2)_2+2H_2O]$, *at +185° C.*

Group.	Series.	μ	$1/\mu \times 10^3$	Int.	Group.	Series.	μ	$1/\mu \times 10^3$	Int.
3	E	0.6158	1623.9	d.	7	A	0.5166	1935.7	vd.
	F	.6133	1630.5	m.		B	.5149	1942.3	d.
4	E	.5860	1706.6	m.		C	.5130	1949.2	d.
	E′	.5849	1709.8	m.		C′	.5122	1952.0	vd.
	F	.5825	1716.8	s.		D	.5107	1958.0	vd.
5	B	.5648	1770.5	vd.		E_1	.5096	1962.3	d.
	C′	.5630	1776.1	vd.		E	.5090	1964.6	m.
	E_1	.5583	1791.2	vd.		F_1	.5075	1970.4	s.
	E	.5575	1793.6	m.		F	.5067	1973.5	s.
	F	.5550	1801.9	s.		F′	.5059	1976.7	vd.
	F″	.5529	1808.8	vd.		G	.5027	1989.1	vd.
	G	.5504	1816.9	vd.		H	.5005	1998.2	vd.
	H	.5473	1827.0	vd.	8	A	.4962	2015.3	d.
	I	.5442	1837.6	vd.		B	.4930	2028.5	m.
6	A_1	.5416	1846.4	vd.		C	.4913	2035.5	m.
	B	.5385	1857.0	d.		C′	.4904	2039.2	d.
	C	.5367	1863.3	d.		D	.4892	2044.1	d.
	C′	.5357	1866.7	vd.		F_1	.4863	2056.3	m.
	D	.5342	1872.1	vd.		F	.4857	2058.7	m.
	E_1	.5329	1876.5	d.		F′	.4848	2062.7	s.
	E′	.5322	1878.9	m.		G	.4823	2073.2	vd.
	F	.5305	1885.0	vd.					
	F′	.5300	1886.7	s.					
	F′	.5289	1890.7	vd.					
	G	.5258	1901.9	vd.					
	H	.5231	1911.7	vd.					

purpose group 7, which is in the brightest part of the spectrum and is free from the complications due to the overlapping of fluorescence and absorption in the reversing region, is most favorable. In figure 82 the spectral region of this group is plotted for the anhydrous and crystalline forms of the single acetate to depict the remarkable displacements brought about by the presence of water of crystallization and the consequent modification of crystal structure. The effect is very similar, both as regards the direction of the shift of the groups and the amount of shift, to that already described in the case of the nitrates. (Compare fig. 78 in Chapter VII.)

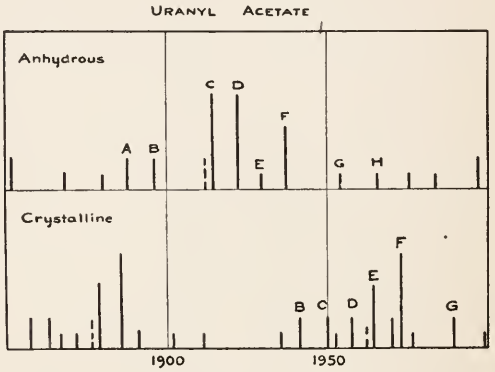

FIG. 82.

In both instances it is not the transfer of the groups toward the blue without change in their structure that occurs, but something much less obvious. In fact, it is not possible to identify any of the bands in the spectra of the hydrated form with those belonging to the anhydrous salt.

To produce this change in the spectrum it is only necessary to add a drop of water to a small portion of the anhydrous powder and to compare the fluorescence of the dry and moistened substance when excited in the usual way at $-185°$.

FREQUENCY INTERVALS OF THE SINGLE ACETATES.

The frequencies and frequency intervals of the series occurring in the spectra of the two forms of the single acetates are given in tables 56 and 57, from which it will be seen that the two forms of the acetate

TABLE 56.—*Uranyl acetate (anhydrous).*

Series.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Average interval.
A	.....	1717.5	1802.6	1888.5	1975.4	85.97
B	.....	1724.3	1810.5	1896.6	1983.6	86.40
C_1	.....	1739.4	1824.6	1912.5	1997.4	86.00
C	1656.4	1742.6	1828.5	1914.4	2000.6	86.00
D	1663.5	1750.5	1836.4	1922.4	2008.6	86.27
E	1673.6	1758.5	1843.6	1929.4	2015.6	85.50
F	1680.6	1765.7	1851.5	1937.5	2024.3	85.91
G	.....	.....	1868.5	1954.4	.....	85.90
H	.....	.....	1880.5	1965.5	.....	85.00
General average	.....	.....	.....	.....	.....	85.96

appear to have the same interval. The difference between the weighted averages is much less than the uncertainties in the determination of the intervals of the dim bands of the weaker series.

TABLE 57.—*Uranyl acetate (crystalline; $2H_2O$).*

Series.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A_2						2015.3	
A_1				1846.4			
A					1935.7		
B			1770.5	1857.0	1942.3	2028.5	86.0
C			1776.1	1863.3	1949.2	2035.5	86.45
C′				1866.7	1952.5	2039.2	86.25
D				1872.1	1958.0	2044.1	86.0
E_1		1706.6	1791.2	1876.5	1962.3		85.23
E	1623.9	1709.8	1793.6	1878.9	1964.6		85.18
F_1				1885.0	1970.4	2056.3	85.65
F	1630.5	1716.8	1801.9	1886.7	1973.5	2058.8	85.66
F′				1890.7	1976.7	2062.7	86.00
F″			1808.8				
G			1816.9	1901.9	1989.1	2073.2	85.42
H			1827.0	1911.7	1998.2		85.60
I			1837.6				
General average							85.72

THE DOUBLE ACETATES.

The fluorescence spectra of these salts have as a rule lower frequency intervals than the two forms of single acetate. The average interval is below 85, as compared with 85.7 for $UO_2(C_2H_3O_2)_2 2H_2O$ and 85.9 for the anhydrous single acetate.

The group structure is in general less symmetrical than that of the double chlorides or the double nitrates and precise comparisons are therefore more difficult.

Corresponding groups in the majority of cases, however, occupy very nearly the same position in the spectrum, and the system of designating the various bands employed in the discussion of the chlorides and nitrates has been used.

If we neglect some of the weaker outlying bands, the group structure of several of the double acetates is found to consist of 4 nearly equidistant bands the wave-length of which is almost if not quite independent of the metal which enters into the composition of the double salt. The substances which most nearly conform to this type are the double acetates containing lithium, potassium, calcium, and strontium.

Manganese uranyl acetate differs from these only in the absence of band B in some groups. (See fig. 83.)

In the spectrum of the barium double acetate the groups are shifted bodily toward the red about 5 frequency units. In the spectra of the ammonium and rubidium salts band D is doubled.

The double acetates of sodium, magnesium, zinc, silver, and lead (fig. 84, *a*) are made up of groups which, while they overlap, are by no means identical, either as to the location or arrangement of their bands.

The spectra of these 5 salts agree, however, in this: They contain in each group 5 bands which correspond so closely with the bands B, C, D, E, and F of the double acetates depicted in figure 83 that by a bodily shift of the group as a whole they may be made to conform to the uniform arrangement, so far as those bands are concerned, quite as well as do the latter. This may be seen from figure 84 *b*, in which the dotted vertical lines indicate the positions of the bands in the uniform type, while the group in each case has been shifted so as to register approximately.

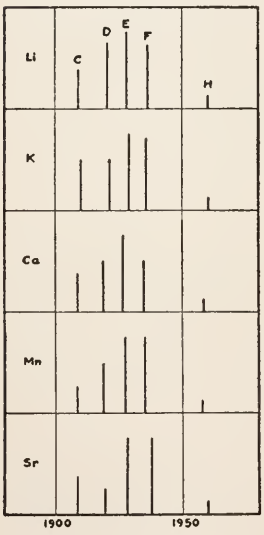

Fig. 83.

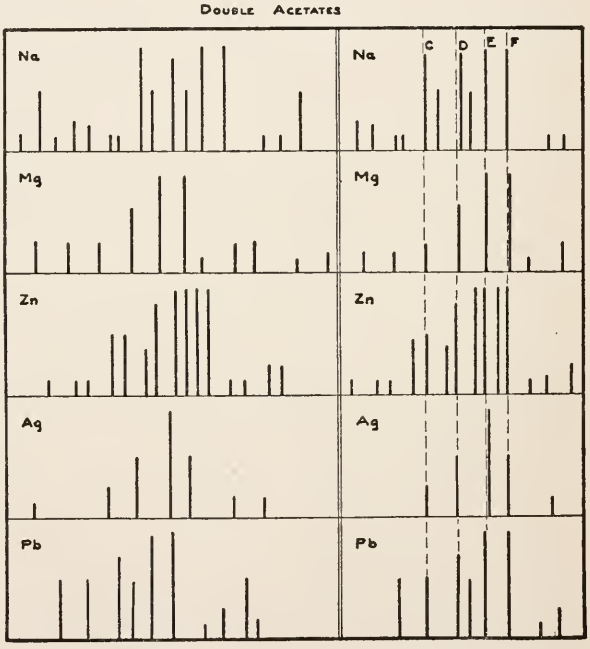

Fig. 84*a*. Fig. 84*b*.

The distinction between the spectra under discussion and those previously considered, which were described as having group spectra conforming to an essentially uniform type both as to location of bands and group-structure, is twofold: (*a*) there is a shift of the groups as a whole; (*b*) there are additional series, varying in intensity, some of which are among the strongest in the spectra and which are characteristic of the individual salt.

It should be reiterated in this connection that neither the bands B, C, D, E, and F, which, although sometimes uniformly shifted, are common to the spectra of the double acetates, nor the additional bands, are found in the spectra of the single acetates. The spectrum of neither the anhydrous acetate nor the crystalline form can be made to conform to the uniform type by a general shift.

A Possible Relation to the Metallic Spark Spectra.

It appears from the foregoing that any metal capable of forming a double uranyl acetate modifies the constitution of the fluorescence spectrum both as to the composition of the groups and their location. Certain metals, such as lithium, potassium, calcium, manganese, and strontium, produce one and the same modification, irrespective of the metal which is present. Other metals shift the group slightly (*e. g.*, barium) or vary slightly the relative distances between neighboring bands without otherwise changing the structure of the group. The presence of still other metals, such as sodium, magnesium, zinc, silver, and lead, results in a considerable general shift and the introduction of new series into the spectrum characteristic of the particular metal in question and existing only in the doublet salt of which it forms a part. Some of these groups are much more complex than the uniform type depicted in figure 83. The others are accompanied by strong bands or minor groups of bands lying outside the usual boundaries.

Fig. 85.

One might imagine, to account for this type of spectrum, that in addition to the metal in combination as a part of the double salt, there are in solution certain other radiators. If these are uncombined particles of the metal existing in a condition akin to the gaseous state, one might expect a type of radiation, under excitation, similar to that discovered by Wood[1] in sodium-vapor; *i. e.*, series of constant frequency made up of bands instead of lines because of damping. One member of each such series should coincide or nearly coincide with some line in the arc or spark spectrum of the metal.

Now, there are in fact various coincidences or approximations thereto close enough to bring lines of the emission spectrum well within the brighter portion of one of the fluorescence bands in question. In the spectrum of silver uranyl acetate, for example, there is a strong series which does not coincide with any series in the fluorescence spectra of the other acetates thus far observed. One member of this series coincides with the brightest visible line in the spark spectrum of silver (Haschek 0.54655 μ; frequency number 1,829.6). Our reading of the corresponding band, made before we had any suspicion of the possible relation here suggested, was 1,829.8. The rather bright line (0.51838) and the neighboring doublet (0.51729–0.51675) in the spark spectrum of magnesium correspond similarly to bands 1,928.9 and 1,934.4 of the fluorescence spectrum.

[1] R. W. Wood. Physical Review (2), xi, p. 76.

In the spark spectrum of lead, of the 9 lines listed by Haschek which lie in the fluorescence region, 7 are within one frequency unit of our readings of the corresponding bands; 4 of these are in practically perfect coincidence, the departures from the crests of the bands being only one or two tenths of a unit.

Of the 25 spark lines of zinc within the fluorescence region, 15 are certainly not related to fluorescence in the manner here under consideration, 4 in somewhat doubtful coincidence, and 6 are in close approximation. Of these last, 5 are consecutive lines of the spark spectrum, all of which are in group 7 of our fluorescence system. The evidence of any significant relation based upon these coincidences is obviously far from conclusive. The matter is mentioned here solely in view of possible developments in the further study of the connection between fluorescence and temperature radiation.

The search for possible coincidences in the case of sodium led to the discovery of a striking arrangement, which seems to be peculiar to that element. The doublets and triplets of the spark spectrum, while they do not form constant-frequency series, are so located that they could be excited to radiation of the type described by Wood, with a common interval equal to the fluorescence interval of the acetates; *i. e.*, about 85, the result would be a well-defined group spectrum of the type of the fluorescence spectrum of the uranyl salts. (See fig. 85.) There are, however, only two individual coincidences with bands of the sodium uranyl acetate.

In the figure, the actual arc-lines of sodium are elongated. The shorter lines are derived from them by assuming constant-frequency series having the interval 85, as described above.

Fluorescence Series in the Spectra of the Double Acetates.

In tables 58 to 70 the fluorescence bands in the spectrum of the double salts are arranged in the order of their wave-length. In tables 71 to 83 the frequencies and average intervals of each series in the various salts are given. It will be seen by comparison with tables 56 and 57 that the average interval for the double acetates is less by more than one frequency unit than for the single acetates; also that the average for the various double salts differ from the general average of all (table 84) by an amount no greater than the difference between the intervals of the various series present in the spectrum of a given salt. In brief, whatever real differences may exist are too small to be determined from our data.

TABLE 58.—*Lithium uranyl acetate.*

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
3 A	0.6105	1638.0	d.	5 C	0.5481	1824.5	m.	7 C	0.5016	1993.7	m.
3 G	.6033	1657.4	vd.	5 D	.5451	1834.4	d.	7 D	.4987	2005.1	s.
3 E	.5963	1677.0	m.	5 E	.5423	1844.0	s.	7 E	.4967	2013.1	ms.
3 H	.5858	1707.0	vd.	5 F	.5399	1852.0	m.	7 F	.4948	2021.1	ms.
4 C	.5740	1742.1	d.	5 G	.5363	1864.7	vd.	7 H	.4889	2045.6	d.
4 D	.5711	1751.0	d.	5 H	.5336	1874.1	vd.	8 C	.4808	2080.0	ms.
4 E	.5680	1760.5	m.	6 C	.5238	1909.0	m.	8 D	.4784	2080.5	s.
4 F	.5653	1769.0	d.	6 D	.5209	1919.8	s.	8 F′	.5751	2104.8	ms.
4 H	.5590	1789.0	vd.	6 E	.5184	1928.9	s.				
				6 F	.5166	1935.8	m.				
				6 G	.5128	1950.2	vd.				
				6 H	.5102	1960.2	d.				

TABLE 59.—*Sodium uranyl acetate.*

2 G	0.6262	1597.0	d.	$5 B_1$	0.5510	1815.0	vd.	7 B	0.5027	1989.2	vd.
2 I	.6107	1637.5	s.	5 B	.5494	1820.2	vd.	7 C	.4998	2001.0	m.
$3 B_1$	.6085	1643.5	m.	5 C	.5468	1828.8	m.	7 C′	.4988	2004.9	d.
3 B	.6068	1648.0	d.	5 C′	.5452	1834.1	m.	7 D	.4972	2011.3	vs.
3 C	.6028	1659.0	d.	5 D	.5432	1840.9	m.	7 D′	.4965	2014.2	vs.
3 C′	.6007	1664.8	d.	5 D′	.5422	1844.3	m.	7 E	.4949	2020.8	s.
3 D	.5978	1672.8	d.	5 E	.5404	1850.6	s.	7 F	.4931	2028.0	s.
3 E	.5948	1681.1	s.	5 F	.5383	1857.8	m.	7 F′	.4917	2033.6	vvd.
3 F	.5924	1688.0	m.	5 F′	.5371	1862.0	vvd.	7 G	.4900	2040.9	d.
3 G	.5898	1695.5	vd.	$5 G_1$	.5359	1866.0	vvd.	7 G′	.4891	2044.5	vd.
3 G′	.5875	1702.0	vvd.	5 G	.5345	1871.0	vd.	7 H	.4874	2051.5	m.
3 H	.5846	1710.5	d.	5 G′	.5332	1875.5	vd.	7 I	.4844	2064.3	vd.
3 I	.5805	1722.5	m.	5 H	.5313	1882.0	m.				
				5 I	.5283	1893.0	vd.	$8 B_1$	.4821	2074.1	vd.
4 B	.5782	1729.5	d.	5 I′	.5269	1897.8	vd.	8 C	.4796	2085.1	s.
4 B′	.5764	1735.0	d.					8 C′	.4787	2089.2	d.
4 C	.5731	1744.9	m.	6 B	.5249	1905.0	vd.	8 D	.4769	2097.0	s.
4 C′	.5717	1749.0	m.	6 B′	.5242	1907.5	vvd.	8 D′	.4762	2100.0	s.
4 D	.5693	1756.5	m.	6 C	.5221	1915.3	s.	8 E	.4734	2112.5	m.
4 D′	.5687	1758.5	m.	6 C′	.5210	1919.3	m.	8 G	.4707	2124.5	vvd.
4 E	.5662	1766.1	s.	6 D	.5191	1926.3	s.				
4 F	.5642	1772.5	m.	6 D′	.5182	1929.9	m.				
4 F′	.5625	1777.8	vvd.	6 E	.5166	1935.6	vs.				
$4 G_1$	.5614	1781.4	vvd.	6 F	.5148	1942.5	vs.				
4 G	.5599	1785.9	vd.	6 G	.5115	1955.0	vd.				
4 G′	.5590	1789.0	vd.	6 G′	.5099	1961.0	vd.				
4 H	.5565	1796.9	m.	6 H	.5083	1967.5	m.				
4 I	.5529	1808.6	d.	6 I	.5048	1980.8	d.				

TABLE 60.—*Magnesium uranyl acetate.*

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 I	0.6147	1627.0	m.	5 A	0.5537	1806.1	d.	7 A	0.5063	1975.1	vvd.
				B	.5507	1815.9	d.	B	.5036	1985.8	m.
3 A	.6115	1635.4	m.	C	.5475	1826.5	m.	C	.5007	1997.1	m.
B	.6072	1647.0	vd.	D	.5447	1836.0	vs.	D	.4983	2006.8	m.
D	.6002	1666.1	m.	E	.5423	1844.0	s.	E	.4966	2013.8	s.
E	.5971	1674.8	d.	F	.5408	1879.0	vvd.	F	.4951	2019.6	vd.
G	.5926	1687.6	vd.	G	.5382	1858.0	d.	G	.4929	2028.7	d.
H	.5897	1695.7	vd.	H	.5358	1866.5	d.	H	.4908	2037.4	d.
I	.5831	1715.0	m.								
				6 A	.5289	1890.8	vd.	B	.4828	2071.4	m.
4 A	.5810	1721.2	d.	B	.5261	1900.9	d.	C	.4802	2082.6	m.
B	.5774	1731.8	vd.	C	.5230	1912.0	m.	D_1	.4791	2087.1	m.
D	.5708	1751.8	s.	D	.5206	1920.9	s.	8 E	.4764	2099.0	m.
E	.5684	1759.2	m.	E	.5184	1928.9	d.	F	.4754	2103.6	d.
F	.5672	1763.2	vd.	F	.5170	1934.4	vd.	G	.4733	2112.6	d.
G	.5640	1773.1	vd.	G	.5145	1943.8	d.	H	.4707	2124.5	d.
H	.5613	1781.6	d.	H	.5128	1950.1	d.				
I	.5556	1799.8	d.								

TABLE 61.—*Ammonium uranyl acetate.*

3 A	0.6097	1640.2	m.	5 B	0.5520	1811.5	d.	7 B	0.5048	1981.0	d.
C	.6044	1654.5	vd.	C	.5484	1823.5	m.	C	.5020	1992.0	m.
E	.5970	1675.5	m.	D′	.5453	1834.0	m.	D′	.4994	2002.5	s.
F	.5945	1682.0	d.	E	.5424	1843.5	s.	D″	.4983	2007.0	s.
I	.5867	1704.5	.....	F	.5404	1850.5	m.	E	.4970	2012.0	s.
				G	.5379	1859.2	vd.	F	.4953	2019.0	s.
4 B	.5789	1727.5	vd.	H	.5360	1865.5	vd.	G	.4929	2029.0	d.
C	.5749	1739.3	d.	I	.5338	1873.5	d.	I	.4897	2042.0	d.
D′	.5709	1751.5	d.								
E	.5681	1760.3	d.	6 B	.5271	1897.0	vd.	8 C	.4816	2076.5	m.
F	.5661	1766.5	m.	C′	.5242	1907.5	m.	D′	.4787	2089.0	vs.
H	.5613	1781.5	d.	D′	.5212	1918.5	m.	D″	.4778	2093.0	vs.
I	.5589	1789.2	vd.	D″	.5200	1923.0	m.	F	.4756	2102.5	m.
				E	.5189	1927.0	s.				
				F	.5171	1934.0	m.				
				G	.5142	1944.8	vd.				
				H	.5127	1950.5	vd.				
				I	.5105	1958.9	d.				

TABLE 62.—*Potassium uranyl acetate.*

3 A	0.6009	1641.2	m.	5 B	0.5512	1814.2	vd.	7 B	0.5041	1983.9	vvd.
C	.5975	1673.7	d.	C	.5484	1823.4	m.	C	.5016	1993.8	s.
E	.5958	1673.5	m.	D	.5444	1837.0	m.	D	.4986	2005.7	s.
F	.5936	1684.7	d.	E	.5420	1845.0	s.	E	.4967	2013.3	s.
H	.5858	1707.8	vd.	F	.5399	1852.2	m.	F	.4948	2021.0	vs.
				H	.5330	1876.0	d.	G	.4923	2031.3	d.
4 C	.5738	1742.8	d.					G′	.....	2036.7	d.
D	.5701	1754.0	d.	6 B	.5262	1900.3	vd.	H	.4891	2044.7	d.
E	.5677	1761.5	m.	C	.5237	1909.3	m.				
F	.5652	1769.1	d.	D	.5202	1922.3	m.	8 C	.4811	2078.9	s.
G′	.5614	1781.3	vd.	E	.5182	1929.6	s.	D	.4781	2091.5	s.
H	.5582	1791.3	d.	F	.5163	1937.0	s.	F	.4749	2105.9	s.
				G	.5138	1946.3	vd.	G	.4724	2116.8	vd.
				G′	.5121	1952.7	vd.				
				H	.5101	1960.4	d.				

TABLE 63.—*Calcium uranyl acetate.*

Group and series.	μ	$1/\mu\times10^3$	Int.	Group and series.	μ	$1/\mu\times10^3$	Int.	Group and series.	μ	$1/\mu\times10^3$	Int.
3 C	0.6017	1662.0	d.	5 C′	0.5483	1823.8	d.	7 C′	0.5017	1993.2	m.
3 D	.5987	1670.3	vvd.	5 D	.5451	1834.5	m.	7 D	.4990	2004.0	m.
3 E	.5968	1675.6	d.	5 E	.5427	1842.6	s.	7 E	.4970	2012.1	s.
3 F	.5939	1683.8	vd.	5 F	.5403	1850.8	m.	7 F	.4953	2019.0	s.
3 H	.5869	1703.9	vd.	5 G″	.5361	1865.3	d.	7 G″	.4918	2033.3	d.
3 J	.5821	1717.9	d.	5 H	.5339	1873.0	d.	7 H	.4895	2042.9	d.
4 C	.5740	1742.2	d.	6 C	.5240	1908.4	m.	7 I	.4852	2051.0	vvd.
4 D	.5703	1753.5	d.	6 D	.5212	1918.6	m.	8 C	.4875	2076.8	m.
4 E	.5682	1759.9	m.	6 E	.5190	1926.8	s.	8 D	.4790	2087.7	m.
4 F	.5659	1767.1	d.	6 F	.5169	1934.6	m.	8 F	.4755	2103.0	s.
4 G″	.5612	1781.9	vd.	6 G″	.5130	1949.3	d.	8 G	.4729	2114.6	vd.
4 H	.5590	1788.9	vd.	6 H	.5107	1958.1	d.				
				6 K	.5059	1976.7	vvd.				

TABLE 64.—*Manganese uranyl acetate.*

4 D	0.5718	1748.9	vd.	6 C	0.5240	1908.4	d.	8 C	0.4812	2078.1	m.
4 E	.5692	1757.0	vd.	6 D	.5213	1918.4	m.	8 D	.4786	2089.4	m.
5 C	.5491	1821.0	vd.	6 E	.5187	1927.9	s.	8 F	.4751	2104.8	m.
5 D	.5454	1833.5	vd.	6 F	.5168	1935.0	s.				
5 E	.5428	1842.3	m.	6 H	.5108	1957.9	d.				
5 F	.5408	1849.1	m.	7 C	.5018	1992.8	m.				
5 H	.5339	1873.0	vd.	7 D	.4994	2002.6	s.				
				7 E	.4971	2011.7	s.				
				7 F	.4952	2019.4	s.				
				7 G	.4936	2025.9	vd.				
				7 H	.4895	2042.9	vd.				

TABLE 65.—*Zinc uranyl acetate.*

2 E	0.6288	1590.3	d.	5 D	0.5460	1831.6	vd.	7 A	0.5050	1980.3	vvd.
				5 D′	.5449	1835.0	d.	7 C	.5026	1989.7	m.
3 A	.6234	1640.0	vd.	5 E	.5430	1841.6	s.	7 C′	.5011	1995.8	m.
3 C	.6045	1654.3	vd.	5 E′	.5420	1845.0	m.	7 D	.4998	2000.9	d.
3 E′	.5967	1675.8	m.	5 F	.5411	1848.0	m.	7 D′	.4988	2004.9	s.
3 F	.5942	1682.9	d.	5 F′	.5400	1851.9	m.	7 E	.4977	2009.1	s.
3 G	.5921	1689.0	vd.	5 G	.5382	1858.0	vd.	7 E′	.4965	2014.0	m.
3 H	.5893	1697.0	vvd.	5 H	.5362	1865.0	vd.	7 F	.4957	2017.2	s.
3 I	.5870	1703.6	vd.	5 I	.5342	1872.0	m.	7 F′	.4946	2021.9	s.
				5 J	.5331	1875.9	d.	7 G	.4935	2026.3	vd.
4 A	.5800	1724.0	d.					7 H	.4918	2033.4	vd.
4 B	.5780	1730.1	vd.	6 A	.5275	1895.7	vd.	7 I	.4899	2041.4	d.
4 C′	.5749	1739.3	d.	6 C	.5249	1905.0	d.	7 J	.4888	2045.9	d.
4 E	.5701	1754.0	d.	6 C′	.5238	1909.1	d.				
4 E′	.5685	1759.0	s.	6 D	.5219	1916.1	d.	8 A	.4843	2064.8	vd.
4 F	.5661	1766.6	m.	6 D′	.5209	1919.9	m.	8 C	.4819	2075.1	m.
4 G	.5640	1773.1	vd.	6 E	.5193	1925.6	s.	8 C′	.4809	2079.6	m.
4 H	.5624	1780.6	vvd.	6 E′	.5182	1929.9	m.	8 D	.4795	2085.5	m.
4 I	.5618	1788.0	d.	6 F	.5171	1934.0	m.	8 D′	.4786	2089.3	s.
				6 F′	.5160	1938.0	m.	8 E	.4776	2094.0	m.
5 A	.5528	1809.0	d.	6 G	.5149	1942.0	vvd.	8 F	.4758	2101.9	s.
5 B	.5512	1814.1	vd.	6 H	.5131	1949.1	vvd.	8 G_1	.4746	2107.0	d.
5 C′	.5482	1824.0	m.	6 I	.5110	1956.9	d.				
				6 J	.5099	1961.3	d.				

TABLE 66.—*Rubidium uranyl acetate.*

Group and series.	μ	$1/\mu\times10^3$	Int.	Group and series.	μ	$1/\mu\times10^3$	Int.	Group and series.	μ	$1/\mu\times10^3$	Int.
3 B	0.6093	1641.2	vd.	5 C	0.5489	1821.8	s.	6 H	0.5129	1949.7	vd.
3 E	.5977	1673.1	s.	C′	.5476	1826.2	vd.	6 I	.5109	1957.3	m.
3 F	.5955	1679.3	d.	D	.5458	1832.3	m.				
3 H	.5879	1701.0	vvd.	D′	.5445	1836.5	d.	7 C	.5022	1991.2	s.
				5 E	.5428	1842.3	vs.	7 D	.4995	2002.0	s.
4 A′	.5811	1720.9	vd.	F	.5405	1850.0	s.	7 D′	.4984	2006.4	m.
4 C	.5753	1738.2	m.	G	.5377	1859.8	vd.	7 E	.4971	2011.7	s.
4 C′	.5739	1742.5	vvd.	H	.5360	1865.7	vd.	7 F	.4953	2019.0	s.
4 D	.5717	1749.2	d.	I	.5338	1873.4	s.	7 G	.4927	2029.6	vvd.
4 D′	.5703	1753.3	d.					7 H	.4916	2034.2	vvd.
4 E	.5685	1759.0	vs.	6 C	.5241	1908.0	s.	7 I	.4893	2043.7	m.
4 F	.5662	1766.2	s.	C′	.5229	1912.4	vvd.				
4 G	.5639	1773.4	vvd.	D	.5214	1917.9	s.	8 C	.4813	2077.7	s.
4 H	.5618	1780.0	vvd.	D′	.5202	1922.0	m.	8 D	.4790	2087.7	s.
4 I	.5592	1788.3	m.	E	.5188	1927.5	vs.	8 D′	.4780	2092.1	m.
				F	.5170	1934.2	s.	8 F	.4751	2104.8	s.
5 A	.5554	1800.6	d.	G	.5144	1944.0	vd.	8 G	.4730	2114.2	vd.
5 B	.5525	1810.0	d.								

TABLE 67.—*Strontium uranyl acetate.*

2 I	0.6112	1636.1	d.	5 C	0.5483	1823.9	m.	7 C	0.5017	1993.2	m.
				D	.5453	1834.0	vd.	7 D	.4990	2004.0	m.
3 E	.5974	1674.0	m.	E	.5427	1842.6	m.	7 E	.4969	2012.5	m.
3 F	.5951	1680.5	m.	5 F	.5407	1849.4	m.	7 F	.4950	2020.4	s.
3 H	.5872	1703.0	d.	G	.5363	1864.5	d.	7 G	.4916	2034.0	vd.
3 I	.5812	1720.7	d.	H	.5334	1874.9	d.	7 H	.4888	2045.9	vd.
				I	.5300	1886.8	vd.				
4 C	.5752	1738.6	d.					8 C	.4812	2078.2	s.
4 D	.5721	1747.9	d.	6 C	.5239	1908.6	m.	8 D	.4789	2088.1	m.
4 E	.5687	1758.5	m.	D	.5211	1919.0	d.	8 F	.4751	2105.0	s.
4 F	.5663	1765.8	m.	E	.5187	1928.0	s.				
4 G	.5615	1780.8	vd.	6 F	.5169	1934.5	s.				
4 H	.5589	1789.1	vd.	G	.5131	1949.0	d.				
				H	.5104	1959.1	d.				
				I	.5078	1969.4	d.				

TABLE 68.—*Silver uranyl acetate.*

3 E′	0.5979	1672.5	d.	5 C	0.5500	1818.4	d.	7 C	0.5027	1989.2	d.
3 F	.5961	1677.5	vd.	D	.5465	1829.7	m.	7 D	.5000	2000.2	s.
3 H	.5878	1701.2	vd.	E	.5437	1839.4	s.	7 E	.4979	2008.6	m.
				5 F	.5417	1846.0	m.	7 F	.4960	2016.1	s.
4 A	.5806	1722.5	vd.	G	.5379	1859.0	vd.	7 G	.4930	2028.6	vd.
4 C	.5764	1735.0	d.	H	.5345	1871.0	vd.	7 H	.4902	2040.0	vd.
4 D	.5730	1745.1	d.								
4 E	.5699	1754.7	m.	6 C	.5250	1904.9	d.	8 C	.4824	2073.0	d.
4 F	.5678	1761.1	d.	D	.5227	1913.2	m.	8 D	.4796	2085.1	s.
4 G′	.5625	1777.7	vd.	E	.5198	1923.9	s.	8 F	.4759	2101.5	m.
4 H	.5600	1785.7	vd.	F	.5183	1931.0	m.				
				G	.5141	1945.1	vd.				
				H	.5113	1955.7	vd.				

TABLE 69.—*Barium uranyl acetate.*

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
3 C	0.6055	1651.5	vd.	5 C	0.5498	1818.8	d.	7 C	0.5025	1990.0	d.
E	.5993	1668.6	d.	D	.5471	1827.8	d.	D	.5000	2000.0	m.
F	.5963	1677.0	d.	E	.5441	1837.9	s.	E	.4978	2008.8	m.
G	.5923	1688.3	vd.	F	.5415	1846.7	s.	F	.4959	2016.5	s.
H	.5888	1698.4	d.	G	.5387	1856.3	d.	G	.4933	2027.2	vd.
				H	.5349	1869.5	d.	H	.4901	2024.4	d.
4 C	.5764	1734.9	vd.								
D	.5733	1744.3	d.	6 C	.5250	1904.8	d.	8 C	.4878	2075.5	m.
E	.5700	1754.4	m.	D	.5226	1913.5	m.	D	.4795	2085.5	s.
F	.5672	1763.0	m.	E	.5201	1922.7	s.	F	.4759	2101.3	m.
G	.5638	1773.7	d.	F	.5180	1930.5	s.	G	.4731	2113.7	vd.
H	.5602	1785.1	d.	G	.5150	1941.7	vd.				
				H	.5116	1954.7	d.				

TABLE 70.—*Lead uranyl acetate.*

2 K	0.6202	1621.6	m.	C	0.5489	1821.9	m.	6 I	0.5100	1960.8	vd.
				C′	.5472	1827.5	m.	L	.5089	1965.0	vd.
3 B	.6086	1643.1	vd.	D	.5459	1831.7	s.				
C	.6048	1653.4	vd.	E	.5439	1838.7	s.	B	.5042	1983.5	m.
D	.6015	1662.5	m.	E′	.5423	1844.0	vd.	C_1	.5028	1989.0	vd.
E	.5991	1669.1	m.	5 F	.5410	1848.3	vd.	C	.5019	1992.4	s.
G	.5938	1684.1	vd.	G	.5390	1855.1	d.	C′	.5008	1997.0	s.
I	.5909	1692.4	d.	H	.5369	1862.4	m.	D	.4996	2001.8	s.
H′	.5891	1697.5	vd.	H′	.5352	1868.5	d.	7 E_1	.4983	2006.8	vvd.
I	.5859	1706.8	m.	I	.5333	1875.1	vd.	E	.4976	2009.6	vst.
L	.5841	1712.1	d.	L	.5320	1879.6	vd.	F	.4948	2021.1	vd.
								G	.4936	2025.8	vd.
4 B	.5788	1727.7	d.	B	.5269	1897.8	m.	H	.4916	2034.0	m.
C	.5751	1738.7	d.	C_1	.5252	1904.0	vd.	I	.4886	2046.7	vd.
C′	.5741	1741.8	d.	C	.5242	1907.6	s.				
D	.5722	1747.7	s.	C′	.5230	1911.9	s.	B	.4837	2067.4	m.
E	.5700	1754.3	s.	D	.5219	1916.2	vs.	C_1	.4824	2073.0	vd.
G	.5649	1770.1	d.	6 E_1	.5201	1922.7	vd.	C	.4814	2077.4	s.
H	.5621	1778.9	m.	E	.5195	1925.0	vs.	D	.4790	2087.5	s.
H′	.5611	1782.3	d.	E′	.5186	1928.3	vd.	8 E	.4772	2095.7	s.
I	.5591	1788.7	vd.	F	.5172	1935.0	vd.	E′	.4766	2098.2	vvd.
L	.5567	1796.3	d.	G	.5149	1942.1	d.	F	.4749	2105.9	d.
				H	.5130	1949.1	m.	G	.4737	2111.0	vd.
5 B	.5518	1812.1	m.	H′	.5119	1953.4	vd.				
C_1	.5500	1818.2	vd.								

TABLE 71.—*Lithium uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A	.....	1638.0	.....	.....	.....	.....	.....	.....
C	.....	1657.4	1742.1	1824.5	1909.0	1993.7	2080.0	84.52
D	.....	.....	1751.0	1834.4	1919.8	2005.1	2090.5	84.89
E	.....	1677.0	1760.5	1844.0	1928.9	2013.1	.....	84.03
F	.....	.....	1769.0	1852.0	1935.8	2021.1	.....	84.05
F′	.....	.....	.....	.....	.....	.....	2104.8	.....
G	.....	.....	.....	1864.7	1950.2	.....	.....	85.50
H	.....	1707.0	1789.0	1874.1	1960.2	2045.6	.....	84.65
Gen. av	.....	.....	.....	.....	.....	.....	.....	84.50

TABLE 72.—*Sodium uranyl acetate.*

B_1	.....	1643.5	1729.5	1815.0	.....	.....	2074.1	86.12
B	.....	1648.0	1735.0	1820.2	1905.0	1989.2	.....	86.43
B′	.....	.....	.....	.....	1907.5	.....	.....	.....
C	.....	1659.0	1744.9	1828.8	1915.3	2001.0	2085.1	85.22
C′	.....	1664.8	1749.0	1834.1	1919.3	2004.9	2089.2	84.88
D	.....	1672.8	1756.5	1840.9	1926.3	2011.3	2097.0	84.84
D′	.....	.....	1758.5	1844.3	1929.9	2014.2	2100.0	85.37
E	1597.0	1681.1	1766.1	1850.6	1935.6	2020.8	.....	84.76
F	.....	1688.0	1772.5	1857.8	1942.5	2028.0	2112.5	84.90
F′	.....	.....	1777.8	1862.0	.....	2033.6	.....	85.27
G_1	.....	1695.5	1781.4	1866.0	.....	.....	.....	85.25
G	.....	1702.0	1785.9	1871.0	1955.0	2040.9	2124.5	84.50
G′	.....	.....	1789.0	1875.5	1961.0	2044.5	.....	85.17
H	.....	1710.5	1796.9	1882.0	1967.5	2051.5	.....	85.20
I	1637.5	1722.5	1808.6	1898.0	1980.8	2064.3	.....	85.36
I′	.....	.....	.....	1897.8	.....	.....	.....	.....
Gen. av	.....	.....	.....	.....	.....	.....	.....	85.22

TABLE 73.—*Magnesium uranyl acetate.*

A	.....	1635.4	1721.2	1806.1	1890.8	1975.1	.....	84.93
B	.....	1647.0	1731.8	1815.9	1900.9	1985.8	2071.4	84.88
C	.....	.....	.....	1826.5	1912 0	1997.1	2082.6	85.37
C′	.....	.....	.....	.....	.....	.....	2087.1	.....
D	.....	1666.1	1751.8	1836.0	1920.9	2006.8	.....	85.18
E	.....	1674.8	1759.2	1844.0	1928.9	2013.8	2099.0	84.84
F	.....	.....	1763.2	1849.0	1934.4	2019.6	2103.6	85.10
G	.....	1687.6	1773.1	1858.0	1943.8	2028.7	2112.6	85.00
H	.....	1695.7	1781.6	1866.5	1950.1	2037.4	2124.5	85.76
I	1627.0	1715.0	1799.8	.....	.....	.....	.....	86.40
Gen. av	.....	.....	.....	.....	.....	.....	.....	85.19

TABLE 74.—*Ammonium uranyl acetate.*

A	.....	1640.2	.....	.....	.....	.....	.....	.....
B	.....	.....	1727.5	1811.5	1897.0	1981.0	.....	84.50
C	.....	1654.5	1739.3	1823.5	1907.5	1992.0	2076.5	84.40
D	.....	.....	1751.5	1834.0	1918.5	2002.5	2089.0	84.38
D″	.....	.....	.....	.....	1923.0	2007.0	2093.0	85.00
E	.....	1675.5	1760.3	1843.5	1927.0	2012.0	.....	84.13
F	.....	1682.0	1766.5	1850.5	1934.0	2019.0	2102.5	84.10
G	.....	.....	.....	1859.2	1944.8	2029.0	.....	84.90
H	.....	.....	1781.5	1865.5	1950.5	.....	.....	84.50
I	.....	1704.5	1789.2	1873.5	1958.9	2042.0	.....	84.38
Gen. av	———	.....	.....	.....	.....	.....	.....	84.40

TABLE 75.—*Potassium uranyl acetate.*

Series.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A	1641.2	.....	.....	.....	.....	.....	.....
B	.....	.....	1814.2	1900.3	1983.9	.....	84.83
C	1656.1	1742.8	1823.4	1909.3	1993.8	2078.9	84.56
D	.....	1754.0	1837.0	1922.3	2005.7	2091.5	84.63
E	1673.5	1761.5	1845.0	1929.6	2013.3	.....	84.95
F	1684.7	1769.1	1852.2	1937.0	2021.0	2105.9	84.24
G	.....	.....	.....	1946.3	2031.3	2116.8	85.25
G′	.....	1781.3	1845.0	1952.7	2036.7	.....	85.13
H	1707.8	1791.3	1876.0	1960.4	2044.7	.....	84.26
Gen. av.	.....	.....	.....	.....	.....	.....	84.57

TABLE 76.—*Calcium uranyl acetate.*

Series.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
C	.....	1742.2	1823.8	1908.4	1993.2	2076.8	83.87
C′	1662.0	.....	.....	.....	.....	.....	.....
D	1670.3	1753.5	1834.5	1918.6	2004.0	2087.7	83.91
E	1675.6	1759.9	1842.6	1926.8	2012.1	.....	84.12
F	1683.8	1767.1	1850.8	1934.6	2019.0	2103.0	83.85
G′	.....	.....	.....	.....	.....	2114.6	.....
G″	.....	1781.9	1865.3	1949.3	2033.3	.....	83.80
H	1703.9	1788.9	1873.0	1958.1	2042.9	.....	84.66
I	.....	.....	.....	.....	2051.0	.....	.....
J	1717.9	.....	.....	.....	.....	.....	.....
K_1	.....	.....	.....	1976.7	.....	.....	.....
Gen. av.	.....	.....	.....	.....	.....	.....	83.88

TABLE 77.—*Manganese uranyl acetate.*

Series.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
C	.....	.....	1821.0	1908.4	1992.8	2078.1	85.70
D	.....	1748.9	1833.5	1918.4	2002.6	2089.4	85.12
E	.....	1757.0	1842.3	1927.9	2011.7	.....	84.90
F	.....	.....	1849.1	1935.0	2019.4	2104.8	85.23
G_1	.....	.....	.....	.....	2025.9	.....	.....
H	.....	.....	1873.0	1957.9	2042.9	.....	84.95
Gen. av.	.....	.....	.....	.....	.....	.....	85.19

TABLE 78.—*Zinc uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A	.....	1640.0	1724.0	1809.0	1895.7	1980.3	2064.8	84.96
B	.....	.....	1730.1	1814.1	.....	.....	.....	84.00
C	.....	1654.3	.....	.....	1905.0	1989.7	2075.1	84.16
C′	.....	.....	1739.5	1824.0	1909.1	1995.8	2079.6	85.03
D	.....	.....	.....	1831.6	1916.1	2000.9	2085.5	84.48
D′	.....	.....	.....	1835.0	1919.9	2004.9	2089.3	84.77
E	1590.3	.....	1754.0	1841.6	1925.6	2009.1	2094.0	83.95
E′	.....	1675.8	1759.0	1845.0	1929.9	2014.0	2101.9	85.22
F	.....	1682.9	1766.6	1848.0	1934.0	2017.2	.....	83.80
F′	.....	.....	.....	1851.9	1938.0	2021.9	.....	85.00
G_1	.....	.....	.....	.....	.....	.....	2107.0	.....
G	.....	1689.0	1773.1	1858.0	1942.0	2026.3	.....	84.33
H	.....	1697.0	1780.6	1865.0	1949.1	2033.4	.....	84.20
I	.....	1703.6	1788.0	1872.0	1956.9	2041.4	.....	84.45
J	.....	.....	.....	1875.9	1961.3	2045.9	.....	85.00
Gen. av.	.....	.....	.....	.....	.....	.....	.....	84.51

TABLE 79.—*Rubidium uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A	.....	.....	.....	1800.6	.....	.....	.....	.....
A′	.....	.....	1720.9	.....	.....	.....	.....	.....
B	.....	1641.2	.....	1810.0	.....	.....	.....	84.40
C	.....	.....	1738.2	1821.8	1908.0	1991.2	2077.7	84.88
C′	.....	.....	1742.5	1826.2	1912.4	.....	.....	84.45
D	.....	.....	1749.2	1832.3	1917.9	2002.0	2087.7	84.62
D′	.....	.....	1753.3	1836.5	1922.0	2006.4	2092.1	84.70
E	.....	1673.1	1759.0	1842.3	1927.5	2011.7	.....	84.65
F	.....	1679.3	1766.2	1850.0	1934.2	2019.0	2104.8	85.10
G	.....	.....	1773.4	1859.8	1944.0	2029.6	2114.2	85.20
H	.....	.....	1780.0	1865.7	1949.7	2034.2	.....	84.73
H′	.....	1701.0	.....	.....	.....	.....	.....	.....
I	.....	.....	1788.3	1873.4	1957.3	2043.7	.....	85.13
Gen. av	.....	.....	.....	.....	.....	.....	.....	84.86

TABLE 80.—*Strontium uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
C	.....	.....	1738.6	1823.9	1908.6	1993.2	2078.2	84.90
D	.....	.....	1749.9	1834.0	1919.0	2004.0	2088.1	85.05
E	.....	1674.0	1758.5	1842.6	1928.0	2012.5	.....	84.63
F	.....	1680.5	1765.8	1849.4	1934.5	2020.4	2105.0	84.90
G	.....	.....	1780.8	1864.5	1949.0	2034.0	.....	84.40
H_1	.....	1703.0	.....	.....	.....	.....	.....	.....
H	.....	.....	1789.1	1874.9	1959.1	2045.9	.....	85.60
I	1636.1	1720.7	.....	1886.8	1669.4	.....	.....	83.32
Gen. av.	.....	.....	.....	.....	.....	.....	.....	84.74

TABLE 81.—*Silver uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
A	.....	.....	1722.5	.....	.....	.....	.....	.....
C	.....	.....	1735.0	1818.4	1904.9	1989.2	2073.0	84.50
D	.....	.....	1745.1	1829.7	1913.2	2002.2	2085.1	85.00
E	.....	.....	1754.7	1839.4	1923.9	2008.6	.....	84.63
E′	.....	1672.5	.....	.....	.....	.....	.....	.....
F	.....	1677.5	1761.1	1846.0	1931.0	2016.1	2101.5	84.80
G	.....	.....	.....	1859.0	1945.1	2028.6	.....	84.80
G′	.....	.....	1777.7	.....	.....	.....	.....	.....
H	.....	1701.2	1785.7	1871.0	1955.7	2040.0	.....	84.70
Gen. av	.....	.....	.....	.....	.....	.....	.....	84.74

TABLE 82.—*Barium uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
C	.....	1651.5	1734.9	1818.8	1904.8	1990.0	2075.5	84.80
D	.....	.....	1744.3	1827.8	1913.5	2000.0	2085.5	85.30
E	.....	1668.6	1754.4	1837.9	1922.7	2008.8	.....	85.05
F	.....	1677.0	1763.0	1846.7	1930.5	2016.5	2101.3	84.86
G	.....	1688.3	1773.7	1856.3	1941.7	2027.2	2113.7	85.08
H	.....	1698.4	1785.1	1869.5	1954.7	2040.4	.....	85.50
Gen. av	.....	.....	.....	.....	.....	.....	.....	85.08

TABLE 83.—*Lead uranyl acetate.*

Series.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.	Average interval.
B	.....	1643.1	1727.7	1812.1	1897.8	1983.5	2067.4	84.86
C_1	.....	.....	.....	1818.2	1904.0	1989.0	2073.0	84.93
C	.....	1653.4	1738.7	1821.9	1907.6	1992.4	2077.4	84.75
C′	.....	.....	1741.8	1827.5	1911.9	1997.0	.....	85.07
D	.....	1662.5	1747.7	1831.7	1916.2	2001.8	2087.5	85.00
E_1	.....	.....	.....	.....	1922.7	2006.8	.....	84.10
E	.....	1669.1	1754.3	1838.7	1925.0	2009.6	2095.7	85.32
E′	.....	.....	.....	1844.0	1928.3	.....	2098.2	84.30
F	.....	.....	.....	1848.3	1935.0	2021.1	2105.9	84.40
G	.....	1684.1	1770.1	1855.1	1942.1	2025.8	2111.0	85.38
H	.....	1692.4	1778.9	1862.4	1949.1	2034.0	.....	85.40
H′	.....	1697.5	1782.3	1868.5	1953.4	.....	.....	85.30
I	1621.6	1706.8	1788.7	1875.1	1960.8	2046.7	.....	85.02
L	.....	.....	1796.3	.....	.....	.....	.....	.....
Gen. av	.....	.....	.....	.....	.....	.....	.....	85.12

TABLE 84.—*Summary of average intervals of the double acetates.*

Substance.	Interval.	Substance.	Interval.
$Li(UO_2)(C_2H_3O_2)_3.3H_2O$.....	84.50	$Zn(UO_2)_2(C_2H_3O_2)_6.7H_2O$.....	84.51
$Na(UO_2)(C_2H_3O_2)_3$.....	85.22	$Rb(UO_2)(C_2H_3O_2)_3$.....	84.86
$Mg(UO_2)_2(C_2H_3O_2)_6.7H_2O$....	85.19	$Sr(UO_2)_2(C_2H_3O_2)_6.6H_2O$.....	84.74
$NH_4(UO_2)(C_2H_3O_2)_3$.....	84.40	$Ag(UO_2)(C_2H_3O_2)_3$.....	84.74
$K(UO_2)(C_2H_3O_2)_3$.....	84.57	$Ba(UO_2)(C_2H_3O_2)_6.6H_2O$.....	85.08
$Ca(UO_2)_2(C_2H_3O_2)_6.8H_2O$.....	83.88	$Pb(UO_2)(C_2H_3O_2)_4.4H_2O$	85.12
$Mn(UO_2)(C_2H_3O_2)_4.6H_2O$.....	85.19		
		General average.....	**84.76**

ABSORPTION SPECTRA OF THE ACETATES.

The fluorescence and absorption of the acetates are related to each other in a manner entirely similar to that already established in the case of the other uranyl compounds.

The absorption bands occur in series of constant interval and this interval is much shorter than that of the fluorescence series. Fluorescence and absorption overlap in the reversing region, with numerous coincidences and an interlocking of the fluorescence and absorption intervals. Reversals, both exact and of the well-known displaced type, are more frequent, perhaps, than in any family of uranyl salts as yet studied. A notable example occurs in the spectrum of lead uranyl acetate (see fig. 86).

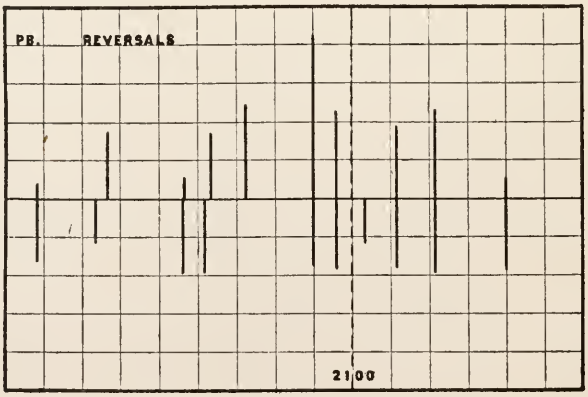

FIG. 86.

The absorption spectra fall into two fairly well defined classes:

(1) Double acetates of Li, NH_4, Na, K, Ca, Zn, Rb, Sr., Ag., Ba.

In this class the system of bands having a series interval of 70+ ends at about 2,180, where is located the head of the strongest series.

Band E of the fluorescence series is usually missing in group 8 and is supplanted by a strong absorption band (1) located 85± frequency

units from the terminating absorption band mentioned above, designated as *e* in accordance with convention used in previous papers.

An excellent example of this type of change from fluorescence to absorption is afforded by the spectrum of barium uranyl acetate (fig. 87). Here an exact reversal of band E_8[1] occurs and the strong absorption band *e*, which takes the place of E in that group, is 85 frequency units from the first member of the strong *e* series which extends toward the ultra-violet with the usual absorption interval of 70 units. Displaced reversals F, G, and H also occur—an indication of the probably complex structure of these bands. The corresponding absorption bands are likewise 85 units from the first members of the *f'*, *g'*, and *h'* series of the absorption spectrum.

There is almost as notable a resemblance between the absorption spectra of this class as between their fluorescence spectra. The resolution is, however, not so good, and all the members of the various series are not so easily located. Almost without exception the bands which can be observed are definitely related, in the manner just described, to the fluorescence series.

(2) The single acetates $UO_2(C_2H_3O_2)_2$ and $UO_2(C_2H_3O_2)_2+2H_2O$; double acetates of Mg, Mn, Pb.

Here the absorption system (interval 70±) distinctly overlaps the fluorescence system extending into the region of groups 8 and 7 beyond, without change of interval.

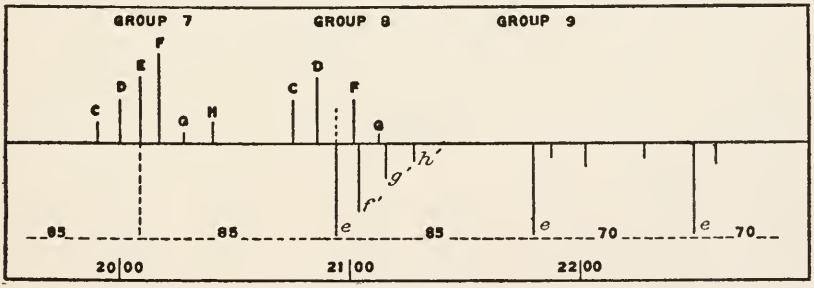

FIG. 87.

The various series of absorption bands located in our visual and photographic studies of the acetates are contained in tables 85 to 97 inclusive. Frequencies and average intervals are given for each salt, the series being designated as usual by small letters, which indicate their relation to fluorescence series denoted by the corresponding capital letter. The three examples of bands or series not thus related to visible fluorescence are indicated by means of the Greek letter γ.

[1] This band E_8 may appear either as fluorescence or as absorption according to the conditions of illumination, etc. It is commonly seen as fluorescence in the spectrum of the zinc uranyl acetate and as absorption in the spectra of other salts of this class.

TABLE 85.—$Li(UO_2)(C_2H_3O_2)_3.3H_2O$.

Series.	Frequencies.						Interval.
c.....	2234.5	2375.0	2446.5	2514.8	2584.8	.....	70.06
c'.....	2085.0	.....	.....	.....	.....	.....	.....
e.....	2097.8	2185.0	2256.6	2325.0	2396.2	.....	70.40
e'.....	2100.0	.....	.....	.....	.....	.....	.....
f'.....	2026.5	2108.8	.....	.....	.....	.....	.....
f''.....	2110.8	.....	.....	.....	.....	.....	.....
g_1.....	2113.0	.....	.....	.....	.....	.....	.....
g.....	2117.8	2201.5	2623.8	.....	.....	.....	70.39
h.....	2124.0	.....	.....	.....	.....	.....	.....
h'.....	2129.0	.....	.....	.....	.....	.....	.....
	Weighted average.....						70.27

TABLE 86.—$NH_4(UO_2)(C_2H_3O_2)_3$.

Series.	Frequencies.						Interval.
β_1.....	2145.6	.....	.....	.....	.....	.....	.....
γ.....	1996.5	2082.4	2163.4	2299.2	2511.6	.....	69.62
c.....	2232.4	2374.0	2446.3	.....	.....	.....	71.73
e.....	2096.2	2183.2	2253.8	2322.8	2394.2	.....	70.12
f'.....	2107.8	.....	.....	.....	.....	.....	.....
g.....	2114.8	.....	.....	.....	.....	.....	.....
h.....	2119.8	2207.0	2278.8	2348.5	2422.8	2487.5	70.13
i'.....	2047.8	2130.0	.....	.....	.....	.....	.....
	Weighted average.....						70.19

TABLE 87.—$Na(UO_2)(C_2H_3O_2)_3$.

Series.	Frequencies.						Interval.
b.....	2229.2	.....	.....	.....	.....	.....	.....
b'.....	2375.3	.....	.....	.....	.....	.....	.....
c.....	2239.6	2311.1	2382.1	2454.0	2524.0	2591.8	69.95
d_1.....	2093.4	.....	.....	.....	.....	.....	.....
d.....	2395.8	.....	.....	.....	.....	.....	.....
e_1.....	2328.3	.....	.....	2472.8	.....	.....	
e.....	2102.6	2190.1	2259.4	2332.1	2403.8	2542.4	70.46
e'.....	2265.0	2336.4	2409.1	2475.9	.....	.....	70.30
f.....	2111.0	2478.9	.....	.....	.....	.....	.....
f'.....	2117.7	2277.4	2343.0	2415.3	.....	.....	70.40
g.....	2126.8	2211.4	2285.7	2350.7	2423.7	2569.1	71.54
h.....	2137.7	2217.8	2291.0	2358.5	2430.1	2499.4	70.15
i.....	2336.3	.....	.....	.....	.....	.....	.....
	Weighted average.....						70.46

TABLE 88.—$Mg(UO_2)_2.(C_2H_3O_2)_6.7H_2O$.

Series.	Frequencies.						Interval.
c_1.....	2161.0	.....	.....	.....	.....	.....	.....
c.....	2168.3	2239.2	.....	.....	.....	.....	70.90
c'.....	2172.8	2315.0	.....	.....	.....	.....	71.10
d'.....	2092.8	.....	.....	.....	.....	.....	.....
e.....	2182.8	.....	.....	.....	.....	.....	.....
f.....	2102.2	.....	.....	.....	.....	.....	.....
g_1.....	2108.4	.....	.....	.....	.....	.....	.....
g.....	2266.0	2336.2	.....	.....	.....	.....	70.20
g'.....	2115.3	2199.3	2269.0	.....	.....	.....	69.70
	Weighted average.....						70.60

TABLE 89.—$K(UO_2)(C_2H_3O_2)$.

Series.	Frequencies.						Interval.
c.....	2166.0	2234.0	.....	.....	.....	.....	68.00
c'.....	2084.0	.....	.....	.....	.....	.....	.....
γ.....	2000.0	.....	.....	.....	.....	.....	.....
d.....	2176.1	.....	.....	.....	.....	.....	.....
e.....	2011.5	.....	.....	.....	.....	.....	.....
e^1.....	2017.0	2100.0	2186.0	2256.3	2326.5	.....	70.25
f_1.....	2025.0	2109.3	.....	.....	.....	.....	.....
g.....	2116.0	2203.0	.....	.....	.....	.....	.....
g'.....	2124.0	2211.6	2292.2	2349.0	.....	.....	68.70
h.....	2131.8	.....	.....	.....	.....	.....	.....
h'.....	2061.8	.....	.....	.....	.....	.....	.....
	Weighted average.....						69.18

TABLE 90.—$Ca(UO_2)_2(C_2H_3O_2)_6.8H_2O$.

Series.	Frequencies.						Interval.
γ.....	2023.1	2092.5	2166.8	.....	.....	.....	71.85
d.....	2173.0	2245.2	2312.7	2384.9	.....	.....	70.63
e.....	2180.1	2249.2	2317.5	2390.1	.....	.....	70.00
f.....	2104.8	.....	.....	.....	.....	.....	.....
f_1.....	2185.0	2254.3	2325.6	2395.8	.....	.....	70.27
g_1.....	2198.8	2340.3	2409.6	.....	.....	.....	70.27
g.....	2032.1	2115.1	2203.6	2274.3	2415.5	.....	70.63
h'.....	2123.6	2278.4	2349.1	.....	.....	.....	70.70
h_1.....	2126.3	.....	.....	.....	.....	.....	.....
i.....	2436.6	.....	.....	.....	.....	.....	.....
	Weighted average.....						70.54

TABLE 91.—$Mn(UO_2)_2(C_2H_3O_2)_6.6H_2O$.

Series.	Frequencies.						Interval.
c.....	2425.0	.....	.....	.....	.....	.....	.....
e.....	2011.5	2094.0	2178.4	2236.2	2307.5	.....	71.62
e^1.....	2311.3	.....	.....	.....	.....	.....	.....
g.....	2110.5	2181.2	2251.5	.....	.....	.....	70.50
	Weighted average.....						71.25

TABLE 92.—$Zn(UO_2)_2(C_2H_3O_2)_6.7H_2O$.

Series.	Frequencies.						Interval.
c.....	2372.5	2442.6	.....	.....	.....	.....	70.10
e.....	2096.4	2181.5	2251.7	2322.9	2392.5	.....	70.10
f'.....	2188.2	.....	.....	.....	.....	.....	.....
g.....	2263.0	.....	.....	.....	.....	.....	.....
h.....	2178.6	2343.6	2415.0	.....	.....	.....	71.40
h'.....	2205.6	2277.9	2350.7	.....	.....	.....	72.80
i.....	2129.9	.....	.....	.....	.....	.....	.....
	Weighted average.....						70.77

TABLE 93.—$Rb(UO_2)(C_2H_3O_2)_3$.

Series.	Frequencies.						Interval.
a.....	2059.3	.....	.....	.....	.....	.....	.....
b_1.....	2070.8	.....	.....	.....	.....	.....	.....
c.....	2158.9	2292.2	2299.4	2373.6	2440.8	.....	70.27
c'.....	2081.6	.....	.....	.....	.....	.....	.....
d'.....	2093.8	2246.7	2317.0	.....	.....	.....	70.35
d''.....	2392.3	.....	.....	.....	.....	.....	.....
e.....	2186.7	2259.4	2326.1	2399.8	.....	.....	71.03
g_1.....	2027.2	.....	.....	.....	.....	.....	.....
g'.....	2115.1	.....	.....	.....	.....	.....	.....
i_1.....	2041.7	.....	.....	.....	.....	.....	.....
i.....	2129.0	2209.5	2279.5	2350.2	2423.1	.....	71.20
	Weighted average.....						70.78

TABLE 94.—$Sr(UO_2)_2(C_2H_3O_2)_6.6H_2O$.

Series.	Frequencies of absorption bands at −185° (groups 8 to 12).						Interval.
c_1.....	2371.2	.....	.....	.....	.....	.....	.....
c.....	2375.6	.....	.....	.....	.....	.....	.....
e_1.....	2390.0	.....	.....	.....	.....	.....	.....
e.....	2094.5R	2181.4	2251.9	2322.5	.....	.....	70.55
e'.....	2185.7	2254.1	.....	.....	.....	.....	68.40
e''.....	2399.9	.....	.....	.....	.....	.....	.....
h.....	2273.8	2412.7	.....	.....	.....	.....	69.45
h'.....	2206.0	2347.8	.....	.....	.....	.....	70.90
i.....	2209.0	2279.1	2350.0	2420.0	2490.0	.....	70.25
	General weighted average.....						70.11

TABLE 95.—$AgUO_2(C_2H_3O_2)$.

Series.	Frequencies.						Interval.
c.....	2231.4	2369.7	.....	.....	.....	.....	69.15
e.....	2180.0	2251.3	2321.2	2390.1	.....	.....	70.03
f'.....	2107.0	2191.4	.....	.....	.....	.....	.....
g.....	2116.0	.....	.....	.....	.....	.....	.....
h.....	2125.0	.....	.....	.....	.....	.....	.....
i.....	2133.0	2204.1	2276.3	2344.7	.....	.....	70.39
	Weighted average.....						70.01

TABLE 96.—$Ba(UO_2)_2(C_2H_3O_2)_6.6H_2O$.

Series.	Frequencies.						Interval.
b.....	2294.1	.....	.....	.....	.....	.....	.....
c.....	2227.2	2370.8	.....	.....	.....	.....	71.82
e.....	2094.7	2180.1	2250.2	2322.5	2393.5	.....	71.13
f'.....	2105.3	2187.2	2260.0	.....	.....	.....	72.80
g'.....	2115.1	.....	.....	.....	.....	.....	.....
gh.....	2204.1	2275.8	2419.0	2486.9	.....	.....	70.70
	Weighted average.....						71.36

TABLE 97.—$Pb(UO_2)(C_2H_3O_2)H_2O$.

Series.	Frequencies.							Interval.
b.....	2065.0	.....	.....	.....	.....	.....	.....	.....
c_1.....	2072.0	2142.5	2355.0	2426.5	2495.0	.....	.....	70.5
c' d.....	2365.0	2437.5	2506.0	.....	.....	.....	.....	71.5
e.....	2094.5	2236.5	2309.8	2380.0	2450.0	2521.0	2594.5	71.43
e'.....	2098.0	2168.5	2240.0	2313.5	.....	.....	.....	71.83
e''.....	2101.5	2389.0	.....	.....	.....	.....	.....	71.87
f.....	2105.5	2176.5	2248.4	2321.5	2392.5	.....	.....	71.75
g.....	2110.5	.....	.....	.....	.....	.....	.....	.....
h.....	2119.5	.....	.....	.....	.....	.....	.....	.....
h'.....	2125.0	2194.5	2264.0	2332.5	.....	.....	.....	71.00
k.....	2201.5	2272.0	2341.0	2413.5	2482.0	2552.5	.....	71.00
	Weighted average.....							71.21

TABLE 98.—*General weighted averages of intervals of absorption series in the spectra of the acetates at −185° C.*

Substance.	Interval.	Substance.	Interval.
$UO_2(C_2H_3O_2)_2$.....	71.04	$Zn(UO_2)_2(C_2H_3O_2)_6.7H_2O$.....	70.77
$UO_2(C_2H_3O_2)_2.2H_2O$.....	72.35	Rb $UO_2(C_2H_3O_2)_3$.....	70.78
Li $UO_2(C_2H_3O_2)_3.3H_2O$.....	70.27	$Sr(UO_2)_2(C_2H_3O_2)_6.6H_2O$.....	70.11
$NH_4UO_2(C_2H_3O_2)_3$.....	70.19	Ag $UO_2(C_2H_3O_2)_3$.....	70.01
Na $UO_2(C_2H_3O_2)_3$.....	70.46	$Ba(UO_2)_2(C_2H_3O_2)_6.6H_2O$.....	71.36
$Mg(UO_2)_2(C_2H_3O_2)_6.7H_2O$....	70.60	$Pb(UO_2)(C_2H_3O_2)_4.4H_2O$.....	71.21
K $UO_2(C_2H_3O_2)_3$.....	69.18		
$Ca(UO_2)_2(C_2H_3O_2)_6.8H_2O$.....	70.54	Av. interval for all acetates..	**70.68**
$Mn(UO_2)_2(C_2H_3O_2)_6.6H_2O$....	71.25		

From the list of general, weighted averages of the intervals for the various salts (tables 97 and 98) it appears that the frequency interval of the single acetates is larger than the general average, corresponding in this respect with the larger interval of their fluorescence spectra, as has been previously noted. The determination of intervals is, however, somewhat less accurate than in the case of the fluorescence bands, and, as in that instance, no difference between various series, or various salts, can be considered as positively established.

Summary.

(1) The spectra of the uranyl acetates consist of the usual equidistant fluorescence bands.

(2) When excitation occurs at the temperature of liquid air, these bands are resolved into groups the homologous members of which form series of constant-frequency intervals.

(3) There are two single acetates—a finely powdered, anhydrous variety and a crystalline form with 2 molecules of water of crystallization, whose spectra differ widely, particularly as to the groups of fluorescence bands.

(4) Of the double acetates, those containing lithium, potassium, calcium, manganese, and strontium have spectra which may be regarded as essentially identical both as regards the location of the principal bands and the structure of the fluorescence groups. The only distinctions between their spectra are in the sharpness of resolution and relative brightness of the various components.

(5) The spectrum of barium uranyl acetate differs from the above in that the groups are shifted, as a whole, about 5 frequency units toward the red.

(6) In the spectra of the double acetates of ammonium and rubidium, band D in each group is doubled, but there is no shift of the groups.

(7) The presence of sodium, magnesium, zinc, silver, and lead modifies the group structure by the addition of bands characteristic of the metal and causes slight relative displacements of the group system as a whole. Otherwise the spectra resemble those mentioned under (4).

(8) The frequency interval for the fluorescence series of the double acetates is probably the same for all series and for all salts, the departures of the general averages for the various salts being less than one frequency unit from the average for all, *i. e.*, 84.76. The same is probably true of the absorption series, the general average for which is 70.68.

(9) The frequency intervals, both in the fluorescence and absorption spectra, are larger by more than one frequency unit for the single acetates than for the double acetates.

IX. THE SULPHATES.

Uranyl sulphate ($UO_2SO_4.3H_2O$) and the double uranyl sulphates of the alkaline metals are among the most brilliant of known fluorescent substances. Their spectra are characterized by an unusual complexity of narrow bands brought out by cooling to the temperature of liquid air. The group structure is by no means so obviously uniform as in the case of the compounds already considered, nor is there the marked similarity between the spectra of the double sulphates which has been noted in the discussion of the fluorescence and absorption of the chlorides, nitrates, and acetates. There are, however, certain characteristics common to all the sulphates thus far examined; *i. e.:*

(1) Fluorescence at $-185°$ vanishes with the group 7 (frequency 2000 to 2070), which is the reversing region for this family of salts, and the eighth group lies entirely within the absorption region.

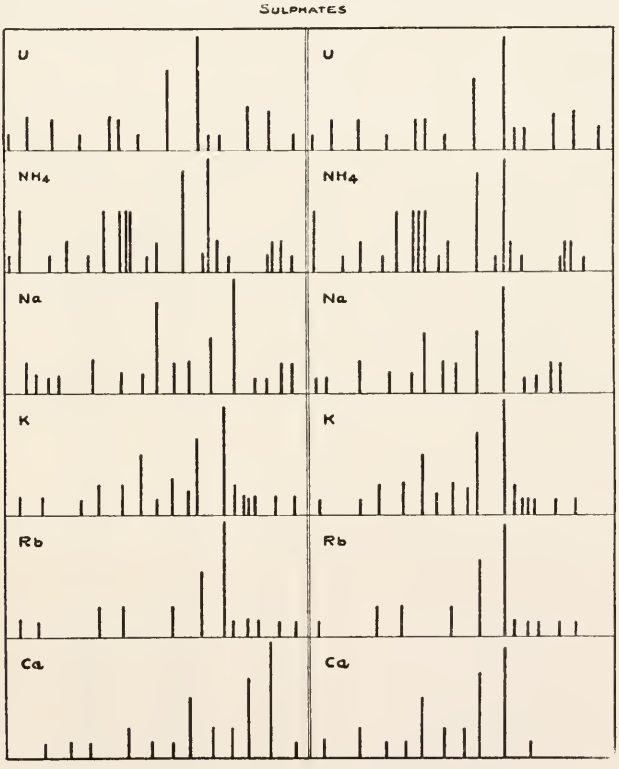

FIG. 88. FIG. 89.

(2) Absorption of the type having the usual 70 ± frequency interval extends *without change of interval* into group 7. In discussing the acetates, what we have called the heads of the prominent absorption series lie in the region between 2040 and 2060 instead of at about 2170, as in the spectra of the acetates.

(3) The fluorescence groups are distinguished by a strong pair of bands, fairly dominant in all the spectra excepting that of the sodium salt. The series formed by the members of shorter wave-length of these pairs terminates toward the violet, where it meets the head of the corresponding absorption series mentioned above.

(4) The location in the spectrum of the fluorescence groups in the spectrum of the sulphates is not approximately the same for the different salts, as is the case with the corresponding double acetates. On the contrary, there is in general a shift toward the violet with increasing molecular weight, as may be seen from figure 88, in which group 5 of the 6 sulphates under consideration are depicted. This shift is larger than that observed in the double nitrates, but not quite so systematic.

TABLE 99.—*Uranyl sulphate: $UO_2.SO_4 3H_2O$. Fluorescence at −185° C.*

Prepared by extracting an excess of uranium oxide (U_3O_8) with sulphuric acid and oxidizing the solution to $UO_2.SO_4$ by means of H_2O_2. This neutral solution was evaporated to crystallization. The crystals were needles, some being 1 by 2 by 5 mm. in size, apparently orthorhombic, with three good pinacoidal cleavages. The angle of the optical axes is very nearly 90° and the double refraction is positive.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 E	0.6254	1599.0	d.	A	0.5256	1902.6	d.
2 F	.6223	1606.9	d.	B	.5237	1909.5	vd.
				B′	.5228	1912.7	vd.
3 B	.6046	1654.0	vd.	C	.5210	1919.4	d.
3 C	.6009	1664.2	vd.	C′	.5203	1921.9	d.
3 D	.5976	1673.4	d.	6 D	.5182	1929.8	d.
3 E	.5942	1682.9	vd.	6 E	.5157	1939.2	m.
3 F	.5914	1691.0	d.	F	.5135	1947.5	s.
3 H	.5857	1707.4	vd.	F′	.5123	1951.8	m.
3 I	.5827	1716.1	vd.	H	.5091	1964.4	m.
				I	.5071	1972.0	d.
4 B	.5740	1742.2	vd.	J	.5054	1978.6	d.
4 C	.5716	1749.4	d.				
4 D	.5686	1758.8	d.	A′	.5027	1989.2	d.
4 E	.5657	1767.7	m.	B	.5014	1994.4	vd.
4 F	.3630	1776.1	m.	B′	.5004	1998.5	m.
4 G	.5600	1785.7	vd.	C	.4990	2004.0	m.
4 H	.5574	1794.1	d.	C′	.4981	2007.6	vd.
4 I	.5551	1801.3	vd.	C″	.4978	2008.8	vd.
4 J	.5534	1807.0	vd.	C‴	.4974	2010.5	vd.
				D	.4964	2014.3	vd.
5 A	.5506	1816.5	d.	7 D′	.4955	2018.2	vd.
5 B	.5478	1825.6	vd.	7 E_1	.4941	2023.9	vd.
5 C	.5450	1834.9	d.	E	.4938	2025.3	m.
5 C′	.5441	1837.9	d.	E′	.4933	2027.2	d.
5 D	.5423	1843.9	vd.	F_1	.4926	2030.0	vd.
5 E	.5394	1853.8	m.	F	.4917	2033.9	s.
5 F	.5369	1862.4	s.	F′	.4912	2035.8	vd.
5 F′	.5357	1866.7	vd.	F″	.4905	2038.7	m.
5 G	.5346	1870.7	vd.	H	.4878	2049.9	m.
5 H	.5321	1879.2	d.	J	.4843	2064.8	vd.
5 I	.5301	1886.4	d.				
5 J	.5280	1893.9	vd.				

If the above groups are aligned by bringing band F into vertical registration, as in figure 89, it will be seen that the apparent dissimilarity in the composition of the group in the various salts is due rather to the occurrence of various weak bands than to the arrangement of the stronger bands, which, while not identical, approximates to identity almost as closely as in the acetates or the nitrates. As in previous diagrams (see the chapters dealing with the spectra of the chlorides, nitrates, and acetates), the vertical lines indicate the position of the crests of the bands and, qualitatively only, their relative intensities. They are estimated in making observations merely as *very strong* (vs),

TABLE 100.—*Uranyl ammonium sulphate:* $(NH_4)_2.UO_2.(SO_4)_2.2H_2O$. *Fluorescence at* $-185°$ C.

Prepared by crystallizing a solution of the two component salts in the proportions of the double salt. The composition has been determined by Rimbach (Ber. d. d. Chem. Ges., 37, 479 (1904); the crystallization by de la Provastaye (Ann. Chem. Phys. (3), 5, 51 (1842), who described it as being monoclinic. The preparation consisted of square and rounded plates of diameter from 0.025 to 0.050 mm. The needle-like crystals showed distinct pleochroism from colorless to yellow, the greatest absorption being in the direction of greatest index.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 E	0.6214	1609.2	d.	5 H_1	0.5300	1886.8	vd.
2 F	.6185	1616.7	d.	5 H	.5295	1888.7	d.
2 H	.6100	1639.3	d.	5 H′	.5290	1890.4	d.
				5 I	.5280	1839.3	vd.
3 B	.6007	1664.7	d.	5 J	.5265	1899.3	vd.
3 C	.5977	1673.1	d.				
3 D	.5941	1683.2	d.	6 A	.5249	1905.2	d.
3 E	.5911	1691.8	s.	6 B_1	.5230	1912.0	vd.
3 F	.5883	1699.7	s.	6 B	.5214	1917.8	d.
3 H	.5809	1721.6	vd.	6 C_1	.5198	1923.8	m.
				6 C	.5194	1925.4	m.
4 A	.5755	1737.6	vd.	6 C′	.5190	1926.8	m.
4 B	.5717	1749.2	d.	6 D_1	.5177	1931.6	d.
4 C	.5697	1755.3	d.	6 D	.5169	1934.6	d.
4 C′	.5689	1757.8	d.	6 E_1	.5152	1941.0	vd.
4 D	.5663	1765.8	m.	6 E	.5147	1943.0	s.
4 E	.5632	1775.5	s.	6 F_1	.5128	1950.1	vd.
4 F	.5608	1783.3	s.	6 F	.5123	1951.9	vs.
4 G	.5579	1792.3	vd.	6 F′	.5116	1954.7	vd.
4 H_1	.5549	1802.1	vd.	6 G_1	.5106	1958.6	vd.
4 H	.5539	1805.5	m.	6 H	.5073	1971.2	vd.
4 J	.5508	1815.5	vd.	6 H′	.5066	1974.0	d.
				6 J	.5038	1984.9	vd.
5 A	.5491	1821.2	d.				
5 B_1	.5472	1827.5	vd.	7 A_1	.5025	1990.0	d.
5 B	.5456	1833.0	m.	7 A	.5015	1994.0	vd.
5 C_1	.5440	1838.2	m.	7 B	.4998	2000.9	d.
5 C	.5435	1840.1	m.	7 C	.4975	2010.0	m.
5 C′	.5430	1841.6	m.	7 D_1	.4960	2016.1	d.
5 D_1	.5415	1846.7	vd.	7 D	.4955	2018.3	d.
5 D	.5406	1849.8	d.	7 E	.4933	2027.1	s.
5 E	.5380	1858.8	s.	7 F_1	.4916	2034.2	vd.
5 F_1	.5361	1865.3	vd.	7 F	.4912	2036.0	vs.
5 F	.5354	1867.6	s.	7 F′	.4905	2038.7	vd.
5 F′	.5346	1870.6	d.	7 G_1	.4893	2043.7	vd.
5 G_1	.5337	1873.7	vd.				

strong (s), *medium* (m), *dim* (d), *very dim* (vd), and *very very dim* (vvd) respectively. No attempt is made in the diagram to indicate the width of the bands.

The spectrum of the single sulphate resembles those of the double sulphates much more nearly than is the case with the single and double salts of the other acids.

Wave-lengths, frequencies, and relative intensities of the bands observed in the fluorescence spectra of uranyl sulphate and the double sulphates of ammonium, sodium, potassium, rubidium, and cæsium are given in tables 99 to 104. Similar measurements of the bands in the absorption spectra are given in table 10. The determination of wave-lengths were made by the visual and photographic methods described in the foregoing chapters.

TABLE 101.—*Uranyl sodium sulphate:* $Na_2.UO_2.(SO_4)_2.2H_2O$. *Fluorescence at −185° C.*

Prepared by crystallizing a solution containing the two component salts in the proportions of the double salt. (See O. de Coninck, Chem. Centralblatt, IX, I, 919, 1905.) The preparation consisted of crystalline grains about 0.5 mm. in diameter, with much mother liquor or deliquescence. The crystals are apparently monoclinic, with positive double refraction.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 B	0.6296	1588.3	vd.	5 D	0.5374	1860.8	d.
2 C	.6255	1598.7	vd.	5 E	.5355	1867.3	d.
2 E	.6182	1617.6	d.	5 F	.5330	1876.0	m.
2 F	.6151	1625.8	m.	5 G	.5311	1882.7	vd.
2 G	.6122	1633.5	vd.	5 G′	.5301	1886.4	vd.
2 H	.6093	1641.2	vd.	5 H	.5287	1891.4	d.
				5 H′	.5278	1894.7	d.
3 B	.5976	1673.3	d.	5 I	.5260	1901.1	d.
3 B′	.5963	1677.0	vd.				
3 C	.5945	1682.1	d.	6 A	.5226	1913.5	d.
3 D	.5908	1692.6	d.	6 B	.5197	1924.2	vd.
3 E	.5880	1700.7	d.	6 C_1	.5181	1930.1	vd.
3 F	.5851	1709.1	s.	6 C	.5167	1935.4	m.
3 G	.5828	1715.9	d.	6 D_1	.5152	1941.0	d.
3 H	.5797	1725.0	d.	6 D	.5141	1945.1	vd.
				6 E	.5123	1951.8	d.
4 A	.5729	1745.5	vd.	6 F_1	.5110	1956.9	vd.
4 B	.5698	1755.1	m.	6 F	.5101	1960.4	s.
4 C_1	.5677	1761.5	vd.	6 G_1	.5087	1965.8	vd.
4 C	.5665	1765.1	m.	6 G	.5077	1969.5	vd.
4 D_1	.5642	1772.4	d.	6 H_1	.5061	1975.9	d.
4 D	.5629	1776.5	d.	6 H	.5050	1980.2	m.
4 E	.5607	1784.1	d.	6 I	.5038	1984.9	vd.
4 F	.5579	1792.3	m.				
4 G	.5560	1798.6	vd.	7 A	.5006	1997.6	vd.
4 H	.5532	1807.7	d.	7 B_1	.4977	2009.2	vd.
4 H′	.5522	1810.9	vd.	7 B	.4965	2013.9	s.
4 I_1	.5509	1815.9	vd.	7 C_1	.4955	2018.2	m.
4 I	.5501	1817.9	vd.	7 C	.4943	2022.9	m.
				7 E	.4910	2036.5	m.
5 A	.5468	1828.8	d.	7 F	.4890	2045.0	d.
5 B	.5439	1838.4	vd.	7 G	.4873	2052.3	vd.
5 C_1	.5418	1845.7	vd.	7 H	.4857	2058.9	d.
5 C	.5406	1849.9	m.	7 H′	.4847	2063.1	vd.
5 D_1	.5388	1856.0	d.				

TABLE 102.—*Uranyl potassium sulphate:* $K_2.UO_2(SO_4)_2.2H_2O$. *Fluorescence at −185° C.*

Prepared by crystallizing a solution of the two component salts in the proportions of the double salt. The composition has been determined by Rimbach (Ber. d. d. Chem. Ges., 37, 478 (1904). The crystals obtained in this laboratory were orthorhombic. The preparation consisted of 6-sided plates and rounded grains about 0.045 mm. in diameter, the plane of the optical axis being *a* (100) and *b* the acute bisectrix. Double refraction positive.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 C	0.6267	1595.7	vd.	5 F′	0.5332	1875.5	d.
2 D	.6229	1605.9	vd.	5 G_1	.5324	1878.3	vd.
2 E	.6188	1616.0	d.	5 G	.5319	1879.9	vd.
2 F	.6164	1622.3	m.	5 G′	.5314	1881.8	vd.
2 F′	.6150	1625.9	vd.	5 H	.5295	1888.6	vd.
2 G	.6129	1631.6	vd.	5 I	.5276	1895.2	vd.
3 B	.6010	1663.9	vd.	6 A′	.5240	1908.4	vd.
3 C_1	.5981	1672.0	d.	6 B_1	.5235	1910.2	vd.
3 C	.5957	1678.8	d.	6 B	.5226	1913.4	d.
3 D_1	.5941	1683.2	vd.	6 C_1	.5199	1923.4	vd.
3 D	.5921	1688.0	vd.	6 C	.5189	1927.2	m.
3 E	.5886	1698.9	vd.	6 D_1	.5173	1933.1	vd.
3 F	.5859	1706.7	m.	6 D	.5164	1936.5	d.
3 F′	.5851	1709.1	d.	6 D′	.5157	1939.1	vd.
3 G	.5830	1715.3	vd.	6 E_1	.5144	1944.0	vd.
3 H	.5804	1723.0	vd.	6 E	.5137	1946.7	m.
4 B	.5718	1748.8	vd.	6 F	.5115	1955.4	s.
4 C_1	.5697	1755.3	d.	6 F′	.5107	1958.1	d.
4 C	.5680	1760.7	d.	6 G_1	.5097	1961.9	vd.
4 D_1	.5662	1766.3	vd.	6 G	.5093	1963.4	m.
4 D	.5644	1771.9	d.	6 G′	.5088	1965.4	vd.
4 E	.5616	1780.5	m.	6 H	.5069	1972.6	d.
4 F	.5589	1789.1	s.	6 I	.5054	1978.6	d.
4 F′	.5583	1791.3	d.	7 A′	.5023	1991.0	m.
4 G	.5563	1797.5	vd.	7 B_1	.5015	1994.0	vd.
4 H	.5539	1805.5	vd.	7 B	.5007	1997.3	d.
4 I	.5519	1811.9	vd.	7 C_1	.4988	2004.7	vd.
5 A′	.5481	1824.5	vd.	7 C	.4973	2010.9	s.
5 B	.5461	1831.0	d.	7 D_1	.4959	2016.5	vd.
5 C_1	.5438	1838.9	d.	7 D	.4951	2019.7	m.
5 C	.5424	1843.8	m.	7 E_1	.4935	2026.5	m.
5 D_1	.5405	1850.1	vd.	7 E	.4923	2031.3	d.
5 D	.5391	1854.9	d.	7 F	.4906	2038.5	s.
5 E_1	.5374	1860.8	vd.	7 G_1	.4894	2043.3	vd.
5 E	.5366	1863.5	m.	7 G	.4889	2045.2	d.
5 F	.5342	1871.8	vs.	7 G′	.4884	2047.5	vd.

TABLE 103.—*Uranyl rubidium sulphate: $Rb_2.UO_2.(SO_4)_3.2H_2O$. Fluorescence at −185° C.*

Prepared by crystallizing a solution containing the two component salts in the proportions of the double salt. The composition has been determined by Rimbach (Ber. d. d. Chem. Ges., 37, 479, 1904). The crystallization is in every way like the potassium salt, although the solubility is less and the crystals smaller. The preparation consisted of 6-sided plates about 0.02 by 0.04 mm. in size.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
1 F	0.6485	1542.0	vd.	5 F′	0.5332	1875.8	vd.
2 C	.6269	1595.1	d.	5 G_1	.5320	1879.7	vd.
2 D	.6225	1606.4	d.	5 G	.5310	1883.2	vd.
2 E	.6187	1616.4	vd.	5 H	.5292	1889.5	vd.
2 F	.6157	1624.1	d.	5 I	.5276	1895.4	vd.
3 B	.6004	1665.5	vd.	6 A′	.5240	1908.4	vd.
3 C	.5975	1673.7	d.	6 B	.5223	1914.5	d.
3 C′	.5954	1699.5	d.	6 C_1	.5198	1923.8	d.
3 D	.5919	1689.5	d.	6 C	.5187	1927.8	m.
3 E	.5887	1698.7	m.	6 D	.5163	1937.0	d.
3 F	.5860	1706.5	s.	6 E	.5136	1946.9	m.
4 B	.5719	1748.5	vd.	6 F	.5115	1955.2	vs.
4 C_1	.5692	1757.0	vd.	6 F′	.5105	1958.7	vd.
4 C	.5679	1760.9	vd.	6 G_1	.5096	1962.3	vd.
4 D	.5643	1772.2	d.	6 G	.5087	1965.8	vd.
4 E	.5616	1780.6	m.	6 H	.5068	1973.3	vd.
4 F	.5591	1788.7	s.	6 I	.5053	1979.0	vd.
4 F′	.5580	1792.0	vd.	7 A′	.5021	1991.8	vd.
4 G	.5560	1798.6	vd.	7 B	.5008	1996.7	d.
4 H	.5538	1805.7	vd.	7 C_1	.4987	2005.2	d.
4 I	.5520	1811.6	vd.	7 C	.4973	2010.9	m.
5 B	.5461	1831.2	d.	7 D	.4953	2018.9	d.
5 C_1	.5438	1838.8	d.	7 E_1	.4930	2028.4	d.
5 C	.5424	1843.7	d.	7 E	.4922	2031.8	d.
5 D	.5392	1854.6	d.	7 F	.4906	2038.4	s.
5 E	.5364	1864.3	m.	7 G_1	.4890	2045.1	vd.
5 F	.5342	1871.8	vs.	7 G	.4880	2049.2	vd.

TABLE 104.—*Uranyl cæsium sulphate:* $Cs_2UO_2(SO_4)_2\ 2H_2O$. *Fluorescence at −185° C.*

Prepared by precipitating uranyl sulphate by adding cæsium sulphate in calculated amount to form the double salt, which is very insoluble. The composition of the crystals is given as above by O. de Coninck (Chem. Centralblat, IX, 1, 1306, 1095). The preparation consisted of very small square plates about 0.01 mm. on a side, the largest of which showed an apparently uniaxial negative figure. The crystals are therefore presumably tetragonal.

Group and series.	μ	$1/\mu \times 10^3$	Int.	Group and series.	μ	$1/\mu \times 10^3$	Int.
2 F	0.6129	1631.8	d.	E_1	.5336	1874.2	d.
				E	0.5321	1879.3	m.
A	.5989	1669.7	vd.	F	.5299	1887.0	s.
B	.5964	1676.7	vd.	5 G	.5276	1895.4	vd.
C_1	.5939	1683.8	d.	G′	.5261	1900.8	vd.
3 C	.5916	1690.3	d.	H′	.5239	1908.6	d.
D	.5894	1696.6	vd.	I	.5228	1912.9	vd.
E_1	.5869	1703.9	vd.				
E	.5850	1709.3	d.	A	.5189	1927.2	d.
F	.5825	1716.6	m.	B	.5168	1935.0	vd.
				C_1	.5148	1942.5	vd.
A	.5695	1755.9	vd.	C	.5140	1945.7	m.
B	.5671	1763.4	vd.	D	.5118	1953.7	vd.
C_1	.5652	1769.2	d.	D′	.5110	1956.9	vd.
C	.5636	1774.3	d.	6 E_1	.5099	1961.0	d.
D	.5612	1782.0	d.	E	.5088	1965.5	m.
4 E_1	.5593	1788.0	d.	F	.5067	1973.6	vs.
E	.5574	1794.0	m.	G	.5047	1981.4	vd.
F	.5550	1801.7	s.	G′	.5035	1986.1	vd.
G	.5517	1812.5	vd.	H	.5019	1992.6	d.
H	.5490	1821.4	vd.	I	.5003	1999.0	m.
I	.5472	1827.4	vd.				
				A	.4970	2012.1	d.
A	.5434	1840.3	d.	C	.4920	2032.6	m.
B	.5410	1848.3	vd.	D	.4902	2040.0	vd.
5 C_1	.5390	1855.2	d.	7 E_1	.4888	2045.8	d.
C	.5374	1860.8	m.	E	.4874	2051.6	m.
D	.5353	1868.0	d.	F	.4858	2058.6	s.

FREQUENCY INTERVALS OF THE FLUORESCENCE SERIES.

The average frequency intervals of the various series, as derived from the foregoing tables, are given in table 105, together with the weighted average for each salt. It will be noted that the intervals of the single sulphate and the double salt of cæsium are distinctly greater than the intervals of the other four sulphates. There is nothing fortuitous about these differences, for, as will be seen from the table, the different series for each salt have intervals within one frequency unit of the general average for that salt, with three exceptions.

These exceptions are series C_1 in the ammonium and sodium double sulphates and G_1 in the ammonium salt. Such occasional apparent discrepancies are not uncommon in the fluorescence spectra of the uranyl salts. They are not due to accidental errors, but are probably ascribable to the complexity of bands having overlapping components the relative intensity of which in different portions of the spectrum varies progressively. Many such cases are known. A doublet ill-resolved and appearing as a single hazy band, the component of longer

TABLE 105.—*Average frequency intervals in the fluorescence spectra of the sulphates.*

Series.	Intervals.		Weighted averages.			
	$UO_2SO_4 + 3H_2O$.	$(NH_4)_2UO_2(SO_4)_2 + 2H_2O$.	$Na_2UO_2(SO_4)3 + 2H_2O$.	$K_2UO_2(SO_4)_2 + 2H_2O$.	$Rb_2UO_2(SO_4)_2 + 2H_2O$.	$Cs_2UO_2(SO_4)_2 + 2H_2O$.
A	.....	84.1	84.0	.....	.....	85.6
A′	.....	.....	.....	83.3	.....	.....
B_1	.....	84.5	.....	.....	.....	.....
B	85.1	83.5	84.2	83.3	82.8	86.1
B′	85.8	.....	84.2	.....	.....	.....
C_1	.....	85.6	85.6	83.2	82.7	86.2
C	.....	84.2	84.8	83.1	83.2	85.6
C′	84.9	84.5	.....	.....	.....	.....
D_1	.....	83.2	84.3	83.3	.....	85.8
D	85.2	83.8	84.2	82.8	82.5	.....
E_1	.....	.....	.....	83.2	.....	85.7
E	85.0	83.6	83.8	82.1	83.1	85.6
F_1	.....	84.4	.....	.....	.....	.....
F	85.4	83.9	83.8	83.3	82.7	85.4
F′	84.6	84.0	.....	83.0	83.3	.....
G_1	.....	85.0	.....	82.5	.....	.....
G	85.2	.....	84.4	82.7	83.5	86.0
G′	.....	.....	.....	82.9	.....	85.3
H_1	.....	84.6	.....	.....	.....	.....
H	85.5	83.0	84.4	83.2	83.8	85.6
H′	.....	83.6	84.1	.....	.....	.....
I	85.2	.....	84.9	83.3	83.7	85.8
J_1	85.2	.....	.....	.....	.....	.....
J	.....	84.7	.....	.....	.....	.....
Average	85.2	83.7	84.3	83.0	83.2	85.7

wave-length being much stronger in the bands toward the red and dying away gradually in subsequent bands as we approach the blue, while the other component steadily increases, will give the effect of an increased frequency interval for the series. The increase might easily be of the general order observed in this case.

There is also always the possibility of the presence of a trace of another uranyl compound which would yield additional series. Such cases, for example, are not uncommon in the study of the acetates, where an admixture of the single acetate occurs.

ABSORPTION SPECTRA.

The difficulties in obtaining a complete record of the absorption bands of the uranyl sulphates are similar to those described in the preceding chapters. The transmission, like that of the other uranyl salts, ranges progressively from almost complete transparency in the red, yellow, and green to a high degree of opacity in the ultra-violet.

Large, clear crystals of the sulphates are not obtainable and therefore it is not possible to use very thick layers and thus to follow the selective absorption far beyond the reversing region toward the red, as has been done in the case of the chlorides.[1] The bands which we were able to locate lie approximately between 2,000 and 2,600 frequency units. They belong almost exclusively to the system having

[1] H. L. Howes. Physical Review (2), XI, p. 66. 1918.

the shorter frequency interval of 70±. A few end members of the reversing system, which presumably extends throughout the fluorescence region, were discernible. Determinations were made in part by photographing the spectrum of the light transmitted by thin layers, in part by the method of reflection.

In table 106 the frequencies of the bands in the spectra of the 6 sulphates are arranged by series. Each series, as usual, is designated by a small letter corresponding to the capital letter which denotes the fluorescence series to which it is related.

TABLE 106.—*Absorption spectra of uranyl sulphates at −180° C.*

Salt.	Series.	Frequencies.					Average interval.
$UO_2SO_4+3H_2O$.	a_1	2056.8	2128.1	2399.8	.....	.....	68.6
	a	2060.6	2202.2	.....	.....	.....	70.8
	b'	2068.7	2140.5	2209.2	.....	.....	70.1
	d_1	2218.3	.....	.....	.....	.....	.....
	d	2016.1	2081.2	2152.9	.....	.....	68.4
	e	2093.6	2160.3	2229.5	.....	.....	68.0
	f_1	2029.9	2170	.....	.....	.....	70.1
	f	2102.6	2236.9	2373.0	.....	.....	70.1
	f'	2035.8	2102.6	.....	.....	.....	.....
	h_1	2045.8	2115.9	2186.7	2327.2	.....	70.3
	h	2260.4	.....	.....	.....	.....	.....
		General average.....					69.6
$(NH_4)_2UO_2(SO_4)_2+2H_2O$.	a	2061.2	2135.3	2205.8	2275.3	.....	71.3
	b	2072.5	2212.4	.....	.....	.....	69.9
	c	2082.8	2155.1	2226.2	2295.2	2510.0	71.2
	d_1	2016.5	(R)2199.8	2263.0	2409.6	.....	69.9
	e	2096.0	2236.2	2305.7	2444.4	.....	69.6
	e'	2031.8	2448.6	.....	.....	.....	69.5
	f_1	2244.4	2315.6	2383.3	2524.0	2595.4	70.2
	f	2107.7	2178.7	2250.0	2454.3	.....	69.3
	f'	2039.6	2253.8	2323.8	2392.0	2464.0	70.4
		.....	.....	.....	.....	2532.8	.....
	g_1	2044.0	2116.0	2187.1	.....	.....	71.5
	g	2330.5	2401.0	2541.0	.....	.....	70.2
	h	2127.7	2198.8	2236.0	2409.6	2477.1	70.3
		.....	.....	.....	.....	2549.4	.....
		General average.....					70.3
$Na_2UO_2(SO_4)_2+2H_2O$.	a	2069.5	.....	.....	.....	.....	.....
	a'	2144.5	2214.7	.....	.....	.....	70.2
	b	2080.8	2153.3	.....	.....	.....	72.5
	c	2093.7	2306.8	2375.9	.....	.....	70.5
	d_1	2167.3	.....	.....	.....	.....	.....
	d	2172.5	2243.8	2314.8	2385.5	.....	71.0
	e	2035.8	2107.5	2250.1	.....	.....	71.4
	e'	2039.2	.....	.....	.....	.....	.....
	f	2043.9	2114.3	2184.5	.....	.....	70.3
	g_1	2050.0	2120.3	2260.4	.....	.....	70.1
	g	2190.1	.....	.....	.....	.....	.....
	g'	2054.7	.....	.....	.....	.....	.....
		2055.2	.....	.....	.....	.....	.....
	h	2063.4	2128.6	2199.9	.....	.....	71.3
	h'	2135.2	2207.7	.....	.....	.....	72.1
		General average.....					71.3

TABLE 106.—*Absorption spectra of uranyl sulphates at −180° C*—continued.

Salt.	Series.	Frequencies.					Average interval.
$K_2UO_2(SO_4)_2 + 2H_2O$.	b_1	2063.1	2412.3	.....	.....	.....	69.8
	b	2064.4	2136.4	2204.6	2276.9	.....	70.8
	b'	2065.7	2341.0	.....	.....	.....	68.8
	c_1	2071.9	2353.5	.....	.....	.....	70.4
	c	2078.6	2289.4	.....	.....	.....	70.2
	d_1	2017.3	2444.1	.....	.....	.....	71.1
	d	2375.3	.....	.....	.....	.....	.....
	d'	2158.2	.....	.....	.....	.....	.....
	e_1	2174.0	.....	.....	.....	.....	.....
	e	2095.5	2307.0	2379.8	.....	.....	71.1
	e'	2241.7	2312.1	2385.0	.....	.....	71.6
	f_1	2035.0	2106.8	2246.7	.....	.....	70.6
	f	2039.6	2109.3	2179.4	2248.2	2390.6	70.2
	f'	2250.7	.....	.....	.....	.....	.....
	g_1	2293.5	.....	.....	.....	.....	.....
	g	2116.4	2188.5	2256.7	2323.7	.....	69.1
	g'	2047.9	.....	.....	.....	.....	.....
	h	2056.8	2266.3	.....	.....	.....	69.8
	General average						70.3
$Rb_2UO_2(SO_4)_2 + 2H_2O$.	b_1	2065.6	2136.6	2205.7	2275.1	.....	69.8
	b	2071.2	.....	.....	.....	.....	.....
	c_1	2218.8	.....	.....	.....	.....	.....
	c	2434.3	.....	.....	.....	.....	.....
	d_1	2014.9	.....	.....	.....	.....	.....
	d	2230.2	2301.0	2443.2	.....	.....	71.0
	d'	2370.5	.....	.....	.....	.....	.....
	e_1	2028.4	2096.2	2375.1	2449.8	.....	70.2
	e	2241.2	2307.3	2378.7	.....	.....	68.8
	e'	2312.2	.....	.....	.....	.....	.....
	f_1	2106.6	2174.5	2249.2	.....	.....	71.3
	f	2037.9	2107.6	.....	.....	.....	69.7
	f'	2040.3	2109.7	2179.4	2385.7	.....	69.1
	g_1	2045.4	2322.0	2391.3	.....	.....	69.2
	g	2048.5	2117.7	2187.7	2256.7	2325.8	69.3
	h_1	2193.9	.....	.....	.....	.....	.....
	h	2085.5	2267.3	2340.8	2408.5	.....	70.0
	General average						69.8
$Cs_2UO_2(SO_4)_2 + 2H_2O$.	a	2096.0	2165.4	2236.9	2375.9	2445.0	70.3
						2517.7	.....
	a'	2311.9	.....	.....	.....	.....	.....
	c	2103.5	.....	.....	.....	.....	.....
	c'	2035.8	2106.4	.....	.....	.....	70.6
	d_1	2115.1	.....	.....	.....	.....	.....
	e	2120.0	2261.0	2329.6	2399.8	2471.0	70.5
		.....	.....	.....	2542.8	2613.4	.....
	f	2061.2	2130.8	2200.6	.....	.....	69.7
	f'	2133.4	.....	.....	.....	.....	.....
	g	2065.5	2206.5	2279.5	.....	.....	71.3
	g'	2071.9	2143.6	2215.8	2353.1	2426.9	70.8
		.....	.....	.....	2498.3	2567.2	.....
	h	2077.2	.....	.....	.....	.....	.....
	i	2084.6	2294.1	.....	.....	.....	69.8
	General average						70.4

TABLE 107.—*Average frequency intervals for the six sulphates.*

UO_2SO_4	69.6	$K_2UO_2(SO_4)_2$	70.3
$(NH_4)_2UO_2(SO_4)_2$	70.3	$RB_2UO_2(SO_4)_2$	69.8
$Na_2UO_2(SO_4)_2$	71.3	$Cs_2UO_2(SO_4)_2$	70.4

As is frequently the case in these absorption spectra, one or more bands of a given series are commonly missing or at least not discernible in the negatives. On the other hand, nearly all the bands are found to be members of a series which is definitely related to a fluorescence series and has the proper frequency interval. The occasional isolated bands, moreover, are so located that they may be definitely associated with a fluorescence series and may reasonably be classed as the sole visible member of an absorption series the remainder of which fails to appear in our photographs.

These show no systematic departure from the general average (70.3) for the entire group. Lying as they do within one frequency unit of the average, we may fairly conclude that within the errors of observation, which are rather large on account of the lack of definition and incomplete resolution of these absorption groups, the various sulphates have a common frequency interval.

The frequency intervals of the various series of a given salt depart somewhat more widely from the average for that salt, but again there is no systematic variation, and it is probable that all the series would be found to have the same interval, were it possible to locate the bands with greater certainty.

SUMMARY.

(1) The fluorescence spectrum of the uranyl sulphates consists of 8 equidistant bands, the first and eighth of which disappear at the temperature of liquid air.

(2) The remaining bands are resolved into groups of narrow line-like bands, the homologous members of which form series having constant frequency intervals, ranging from 85.7 in cæsium uranyl sulphate to 83.0 in potassium uranyl sulphate.

(3) The fluorescence groups are distinguished by a strong pair of bands about 8 frequency units apart and 7 weak bands, some of which are doublets.

(4) There is a shift of all bands toward the violet, with increasing molecular weights, of about 15 frequency units in passing from the spectrum of uranyl sulphate to that of cæsium uranyl sulphate.

(5) The absorption spectra of the sulphates are made up of series of bands having a frequency interval of 70.3 (general average).

(6) These absorption series extend into group 7 of the fluorescence without break of interval. There are many reversals where fluorescence and absorption overlap. The reversing region is therefore one group farther toward the red than in most spectra of the uranyl compounds.

X. THE FLUORESCENCE OF FROZEN SOLUTIONS.

The fluorescence spectra of solutions generally consist of only one or two very broad bands. Such bands undoubtedly possess component bands in considerable number, but spectrum analysis often fails to reveal them because of extensive overlapping. Chlorophyl in alcohol possesses a series of absorption bands[1] which resemble the absorption bands of the uranyl solutions. The very broad fluorescence band in the orange and red probably consists of several components which form a similar series. Anthracene in solution[2] presents a fluorescence series of at least 4 bands which strongly resembles the series found in the fluorescence spectra of uranyl solutions.

Probably the first observer to note the fact that uranyl solutions yield fluorescence spectra consisting of several bands was G. C. Stokes.[3] He states that "a solution of nitrate of uranium is decidedly sensitive," *i. e.*, fluorescent. Later, in the same paper, he writes "I have observed seven of these bands arranged at regular intervals." E. Becquerel,[4] in his monumental work on the uranyl salts, makes this observation:

"Certain solutions of the salts of uranium give, in the violet rays, a luminous emission scarcely less brilliant than the crystals themselves . . . . several [bands] appear to correspond to the bands given by the solid salts; the sulphate and the double sulphate of potassium and uranium are in this class."

In the same year Hagenbach,[5] who was studying many fluorescence materials, observed that the uranyl oxide in nitric acid shows 8 very sharply outlined maxima in the fluorescence spectrum. Morton and Bolton[6] studied the absorption of the uranyl solutions and noted the fluorescence. These investigators were the first to recognize the possibility of the existence of more than one hydrate of the same salt, which, they state, "enables us to explain some discrepancies of authorities on this point." Our present work has brought out the necessity, of such a hypothesis. Jones and Strong,[7] following the same method as Morton and Bolton, have published the most extensive data on the absorption spectra, but their work does not include temperatures below the freezing-point.

This chapter contains the results of experiments which were described in two papers, together with some additional data heretofore unpublished. The first, a preliminary paper,[8] showed that the bands of

[1] Nichols and Merritt. Carnegie Inst. Wash. Pub. No. 130, p. 85. 1910.
[2] Louise MacDowell. Physical Review (1), 26, p. 155. 1908.
[3] Stokes. Philosophical Transactions, p. 463. 1852.
[4] E. Becquerel. Comptes Rendus, 75, p. 296. 1872.
[5] Hagenbach. Poggendorf Annalen, 146, p. 582. 1872.
[6] Morton and Bolton. Chemical News, pp. 113, 164. 1873.
[7] Carnegie Inst. Wash. Pub. No. 130.
[8] Nichols and Merritt. Physical Review (2), 3, p. 457. 1914.

the solutions, even at −180°, resembled in breadth and regular spacing those of the solid salts at room temperature. The uranyl acetate in alcohol proved to be the exception, since at −180° it resolved into faint lines, which did not, however, coincide in position with those of the solid acetate at that temperature.

The variety of shifts with systematic dilution and temperature change led to the second investigation,[1] in the hope that some general law of shift might be deduced. It was also planned to study the fundamental relations between concentration and frequency interval, temperature, and state of resolution, etc. With these relations in view much work was done which led to the discovery of many beautiful and unique spectra.

EXPERIMENTAL METHOD.

For the study of the spectra, except where otherwise specified, a Hilger constant-deviation spectrometer was used.

The apparatus for the cooling and excitation of the substances under observation was designed to enable the observer to hold the temperature of the specimen constant at any temperature between 0° and −180° C. The mounting consisted of a cylindrical copper block *M* (fig. 90), the top of which was bored to receive a small test-tube *F*, which contained the fluorescent solution. The side of the block was channeled to let the exciting light fall on the specimen and to let the fluorescent light out. To the bottom of this copper block was soldered a cylinder of sheet copper, which could be partially or completely covered by the liquid air in the unsilvered Dewar bulb *D*, thus producing different temperatures in the specimen. This mounting was rigidly suspended from above by partially non-

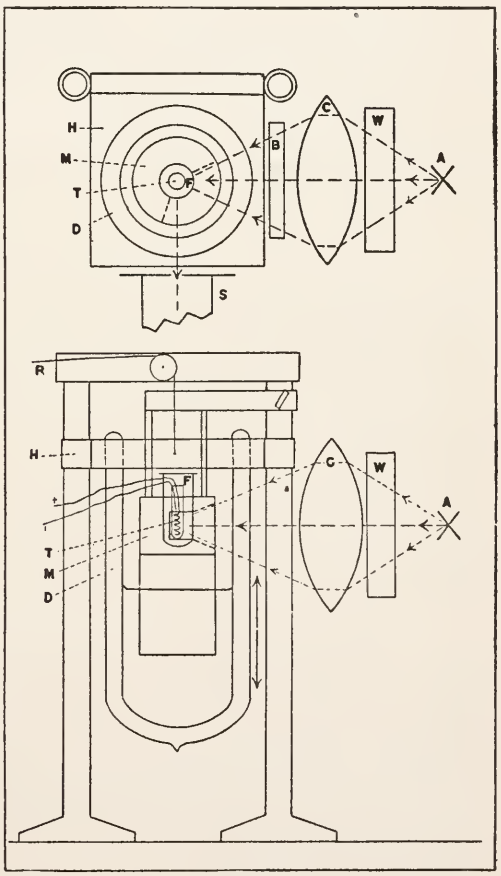

FIG. 90.

[1] Howes. Physical Review (2), vol. 6, p. 193. 1915.

conducting material. The Dewar bulb was fastened to an adjustable support H, and the mounting could be submerged in the liquid air to various depths by raising or lowering the bulb by means of a cord R.

Fluorescence was excited by the rays from a carbon arc A. The light passed successively through a water-cell W, a large short-focused condenser C, and a solution of ammonio-copper sulphate B. This solution absorbed all of the exciting light of a wave-length greater than 0.4780 μ, so that the fluorescent light, which entered the collimator slit S of the spectrometer, could be viewed on a black background. A small resistance coil T was inserted in a glass tube, which was always placed in the middle of the solution. The temperatures were recorded on a Callender recorder. The massive copper block M served to reduce the vertical temperature gradient in the frozen solution to less than 1° per centimeter. It made the apparatus rather slow in responding to changes, but afforded an excellent control of temperature.

The salts were carefully weighed and "normal" solutions were prepared.[1] Acid solutions were made by adding a definite volume of the commercial concentrated acid to a definite volume of a water solution of known concentration.

Although readings were taken and tables made in units of wave-length, the diagrams of spectra are plotted on an arbitrary scale of frequencies, *i. e.*, $1/\mu \times 10^3$.

URANYL SULPHATE IN AQUEOUS SOLUTION.

The uranyl sulphate in water, upon excitation with the carbon arc, yields 4 bands at +20° C.; but when cooled 6 bands are visible, the new bands being of longer wave-lengths. This phenomenon—increase of intensity with cooling—is a very fortunate one, for otherwise the study of the more dilute solutions would be limited to the lowest temperatures. In table 108 will be found the bands of the 1/1, 1/10, 1/100, and 1/1000 normal aqueous solutions. In the spectrum of the 1/1 normal solution band 7 is at 0.4927 μ at +20°, which is of interest because the crystalline salt was found to give a fluorescence band at 0.4925.[2]

If a reasonable error is assumed, these bands may be considered to be coincident. In this region they are approximately 75 Å.U. in width; hence measurements were taken on the crest rather than on the middle of the band, the crests being located slightly nearer the violet edge.

The absorption spectrum[3] of the normal solution presents a band in this region at 0.4910, which is 17 Å.U. nearer the violet than the fluores-

[1] The term "normal" solution, as used in this paper, means one which contains the same number of grams of solute to the liter of solvent as the number which represents the molecular weight of the particular salt dissolved.

[2] Nichols and Merritt. Physical Review (1), 33, p. 354. 1911.

[3] Jones and Strong. Carnegie Inst. Wash. Pub. No. 130, p. 109.

cence band. Jones and Strong employed the continuous spectrum of the Nernst lamp, which produces fluorescence in this region. Such luminescence, although masked by the more intense background, tends to shift the crest of the absorption band toward the violet.

A comparison of the wave-lengths of the bands of the solid with those of the solution indicates a progressive difference. When the spectra of the solution and of the solid are plotted in frequency units, either is found to include only one series of bands, those of the solution being of a slightly smaller interval than those of the solid.

TABLE 108.—*Uranyl sulphate in water.*[1]

Solution and temp.		Band 2.	Band 3.	Band 4.	Band 5.	Band 6.	Band 7.
Normal solution.	+ 20	.....	.....	0.5641	0.5383	0.5143	0.4927
	0	.....	.....	.5641	.5383	.5141	.4926
	− 35	.....	0.5934	.5641	.5378	.5141	.4927
	− 60	0.6229	.5928	.5637	.5376	.5137	.4924
	− 90	.6227	.5923	.5635	.5370	.5131	.4919
	−120	.6230	.5923	.5634	.5370	.5133	.4919
	−150	.6235	.5924	.5634	.5373	.5136	.4919
	−180	.6241	.5924	.5636	.5375	.5140	.4921
1/10 normal solution.	+ 20	.....	.....	.5636	.5379	.5139	.4918
	− 30	.....	.....	.5631	.5373	.5136	.4913
	− 60	.....	.5911	.5629	.5368	.5130	.4911
	− 90	.....	.5904	.5621	.5364	.5125	.4910
	−120	.....	.5904	.5624	.5365	.5127	.4909
	−150	.6228	.5917	.5629	.5367	.5130	.4913
	−180	.6231	.5921	.5633	.5371	.5133	.4916
1/100 normal solution.	− 35	.....	.....	.5633	.5373	.5135	.4913
	− 60	.....	.....	.5634	.5373	.5129	.4911
	− 90	.....	.....	.5631	.5368	.5125	.4907
	−120	.....	.....	.5629	.5365	.5126	.4907
	−150	.....	.5924	.5631	.5368	.5129	.4909
	−180	.....	.5928	.5638	.5370	.5132	.4911
1/1000 normal solution.	− 90	.....	.....	.5583	.5330	.5102	.4904
	−120	.....	.....	.5574	.5324	.5097	.4904
	−150	.....	.....	.5574	.5345	.5105	.4909

[1] The numbers by which unresolved bands are designated in this and the following tables correspond to the group numbers used in previous chapters, since each band corresponds to a group in the resolved spectra of the crystallized salts.

In figure 91, band 5 is seen to shift with falling temperature toward the violet, the shift amounting to 13 Å.U. when a temperature of −100° is reached. With further cooling to −180° the band shifts back toward the red. It would be interesting to ascertain whether this shift toward the red would continue with further decrease in temperature. The other bands of the normal solution behave similarly with falling temperature, *i. e.*, the entire spectrum undergoes a shift to the violet, followed by a reverse shift to the red. The wave-lengths of the bands at −180° are approximately the same as the wave-lengths at −60°.

Jones and Strong discovered a shift of 15 Å.U. toward the red for the *absorption band* of wave-length 0.4910 when the temperature of their solution was raised from +5° to +84°. Our fluorescence band at 0.4927 shifts in the same direction, with a rise in temperature from −90° to +20°.

H. Becquerel believed that any modification of the absorption spectrum is accompanied by a similar change in the fluorescence spectrum, and these shifts lend strength to his generalization.

A brief study of the fluorescence spectra of the 1/10 and the 1/100 normal solutions at different temperatures indicates that a similar temperature shift occurs.

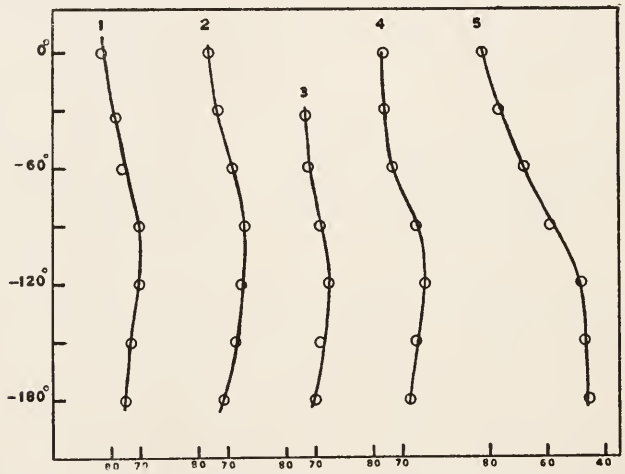

FIG. 91.—Uranyl sulphate—Temperature shift.

(1) 1/1 normal, aqueous: (2) 1/10 normal, aqueous: (3) 1/100 normal, aqueous; (4) 40 c.c. 1/10 normal, aqueous to 1 c.c. sulphuric acid; (5) 1 c.c. 1/10 normal, aqueous to 1 c.c. sulphuric acid.

The increase in the amount of solvent produces a shift of the spectrum toward the violet. For example, band 7 at −90° shifts as follows: in the 1/1 normal solution the wave-length is 0.4919, in the 1/10 normal 0.4910, in the 1/100 normal 0.4907, in the 1/1000 normal 0.4904 μ.

The 1/1000 normal solution shows a spectrum which is very strongly shifted toward the violet. The above comparison of the wave-lengths of band 7 fails to indicate the shift of the spectrum, because it is accompanied by a marked decrease in interval, while of all the bands, number 7 is the least shifted. For example, band 4 of the 1/1000 normal at a temperature of −90° is of wave-length 0.5583, while band 4 of the 1/100 normal at −90° is of wave-length 0.5631 units. Bands 5, 6, and 7 show progressively less variance in wave-length with the corresponding bands of the 1/100 normal solution because of the shorter frequency of the 1/1000 normal interval. Measurements of these spectra plotted on a frequency scale indicate that while the bands are spaced by about 85.7 units in the 1/1, 1/10, and 1/100 normal solutions, the 1/1000

normal bands are of only 82 units interval. (See table 109.) This may be due to a change in the ionization with dilution.

To ascertain whether the rate of cooling caused a change in the spectra, a solution was suddenly plunged into liquid air and excited to fluorescence. Measurements were then taken on the bands, but no change in wave-lengths was observed.

TABLE 109.—*Uranyl sulphate in water. Frequencies and average intervals of fluorescence bands.*

Band.		+20°	0°	−35°	−60°	−90°	−120°	−150°	−180°
Frequencies in normal solution.	2	.....	.....	.....	1605.4	1605.9	1605.1	1603.8	1602.3
	3	.....	.....	1685.2	1686.9	1688.3	1688.3	1688.0	1688.0
	4	1772.7	1772.7	1772.7	1773.9	1774.6	1774.9	1774.9	1774.3
	5	1857.7	1857.7	1857.7	1860.1	1862.2	1862.2	1861.2	1860.5
	6	1944.4	1945.1	1945.1	1946.7	1948.9	1948.2	1947.0	1945.5
	7	2029.5	2030.0	2029.6	2030.9	2032.9	2032.9	2032.1	2030.0
Average int..		85.6	85.8	86.1	85.1	85.4	85.6	85.7	85.5
Frequencies in 1/10 normal solution.	2	.....	.....	.....	.....	.....	.....	1605.6	1604.9
	3	.....	.....	.....	1691.8	1693.8	1693.8	1690.0	1688.9
	4	1774.3	.....	1775.9	1776.5	1779.0	1778.1	1776.5	1775.8
	5	1859.1	.....	1861.2	1862.9	1864.3	1863.9	1863.3	1861.9
	6	1945.9	.....	1947.0	1949.3	1951.2	1950.5	1949.3	1948.2
	7	2033.3	.....	2035.4	2036.2	2036.7	2037.1	2035.4	2034.2
Average int..		86.3	.....	86.5	86.1	85.7	85.8	86.0	85.9
Frequencies in 1/100 normal solution.	3	.....	.....	.....	.....	.....	.....	1688.0	1686.9
	4	.....	.....	1775.3	1774.9	1775.9	1776.5	1775.9	1773.7
	5	.....	.....	1861.2	1861.2	1862.9	1863.9	1862.9	1862.3
	6	.....	.....	1947.4	1949.7	1951.2	1950.8	1949.7	1948.6
	7	.....	.....	2035.4	2036.2	2037.9	2037.9	2037.1	2036.2
Average int..		.....	.....	86.7	87.1	87.3	87.1	87.3	87.3
Frequencies in 1/1000 normal solution.	4	.....	.....	.....	.....	1791.2	1794.0	1794.0	1794.0
	5	.....	.....	.....	.....	1876.2	1878.3	1870.9	1870.9
	6	.....	.....	.....	.....	1960.0	1961.9	1958.9	1958.9
	7	.....	.....	.....	.....	2039.4	2039.4	2037.1	.....
Average int..		.....	.....	.....	.....	82.7	81.8	81.0	82.4

URANYL SULPHATE MIXED WITH SULPHURIC ACID.

It has been observed that the bands of the aqueous solutions move toward the violet with progressive dilution with water; hence it was of considerable interest to ascertain the effect of dilution with sulphuric acid.

The addition of one volume of acid to 40 volumes of the 1/10 normal aqueous solution (table 110) produces a negligible effect, but a mixture of equal volumes shifts the bands back toward the red, in fact, the wave-lengths of the bands at +20° are longer than those of the normal solution—aqueous. This can be discovered from a comparison of the wave-lengths of the 1/10 normal solutions with those of the normal solutions in tables 108 and 110. The effect is not evident at low tem-

peratures, because the spectrum of the 1 to 1 acid solution persistently shifts toward the red instead of reverse shifting at −100° (see fig. 91). The frequency interval remains unchanged, with a proportionately large acid dilution.

TABLE 110.—*Uranyl sulphate in sulphuric acid.*

Temp., etc.		Band 2.	Band 3.	Band 4.	Band 5.	Band 6.	Band 7.
40 c.c. of 0.1 normal aqueous solution with 1 c.c. of acid.	+ 10°	.....	.....	0.5634	0.5376	0.5140	0.4931
	− 30°	.....	0.5929	.5635	.5376	.5139	.4928
	− 60°	0.6238	.5924	.5631	.5373	.5135	.4919
	− 90°	.6224	.5910	5621	.5365	.5129	.4919
	−120°	.6226	.5914	.5625	.5362	.5126	.4920
	−150°	.6234	.5918	.5627	.5365	.5128	.4925
	−180°	.6242	.5919	.5630	.5367	.5130	.4925
1 c.c. of 0.1 normal aqueous solution with 1 c.c. of acid.	+ 20°	.....	.5945	.5657	.5388	.5149	.4921
	− 30°	.6246	.5935	.5640	.5376	.5139	.4916
	− 60°	.6231	.5921	.5630	.5368	.5133	.4911
	− 90°	.6215	.5906	.5616	.5359	.5124	.4905
	−120°	.6199	.5893	.5608	.5348	.5114	.4898
	−150°	.6203	.5893	.5607	.5347	.5113	.4897
	−172°	.6203	.5890	.5602	.5345	.5109	.4893

TABLE 111.—*Uranyl sulphate in sulphuric acid.—Frequencies and average intervals of fluorescence bands.*

Band.		+10°	−30°	−60°	−90°	−120°	−150°	−180°
Frequencies of 40 c.c. of 0.1 normal aqueous with 1.0 c.c. of acid.	2	.....	.....	1603.1	1606.7	1606.2	1604.1	1602.1
	3	.....	1686.7	1688.0	1692.0	1690.9	1689.8	1689.5
	4	1774.9	1774.6	1775.9	1779.0	1777.8	1777.1	1776.1
	5	1860.1	1860.1	1861.2	1863.9	1865.0	1863.9	1863.2
	6	1945.5	1945.9	1947.4	1949.7	1950.8	1950.1	1949.3
	7	2028.0	2029.2	2032.9	2032.9	2032.5	2030.5	2030.5
Average interval...		84.4	85.6	86.0	85.2	85.3	85.3	85.7
Frequencies of 1 c.c. of 0.1 normal aqueous with 1 c.c. of acid.	2	.....	1601.0	1604.9	1609.0	1613.2	1612.1	1612.1
	3	1682.1	1684.9	1688.9	1693.4	1696.9	1696.9	1697.8
	4	1767.7	1773.1	1776.2	1780.6	1783.2	1783.5	1785.1
	5	1856.0	1860.0	1862.9	1866.0	1869.9	1870.2	1870.9
	6	1942.1	1945.9	1948.2	1951.6	1955.4	1955.8	1957.3
	7	2032.1	2034.2	2036.2	2038.7	2041.7	2042.1	2043.7
Average interval...		87.5	86.6	86.3	86.0	85.7	86.0	86.3

URANYL POTASSIUM SULPHATE IN WATER.

The spectra of the aqueous solutions of uranyl potassium sulphate, like those of uranyl sulphate, consist of a single series of bands.

The temperature shift of the more concentrated solutions, *e. g.*, the 1/15 and 1/150 normal, is at first toward the violet, followed by a reverse shift toward the red. The wave-lengths of the bands of the aqueous solutions are recorded in table 112. It will be seen that the shift toward the red is more marked than in the uranyl sulphate solutions. (See also fig. 92.)

The 1/1500 and 1/15,000 normal solutions yield bands which present a hazy appearance, lacking the pronounced crests of the more concentrated solutions. For this reason the readings of such wavelengths are more likely to be in error. The same tendency to first shift toward the violet and then shift toward the red is evident.

TABLE 112.—*Uranyl potassium sulphate in water.*

Solution and temp.		Band 3.	Band 4.	Band 5.	Band 6.	Band 7.
1/15 normal solution.	+ 20°	.....	0.5656	0.5388	0.5154	0.4932
	0°	.....	.5651	.5387	.5152	.4928
	− 30°	0.5942	.5650	.5386	.5148	.4926
	− 60°	.5945	.5652	.5386	.5148	.4927
	− 90°	.5945	.5653	.5386	.5148	.4925
	−120°	.5946	.5653	.5387	.5149	.4928
	−150°	.5953	.5653	.5393	.5154	.4933
	−180°	.5966	.5669	.5406	.5166	.4945
1/150 normal solution.	+ 20°	.....	.....	.5398	.5155	.....
	− 30°	.....	.5659	.5391	.5153	.4931
	− 60°	.....	.5657	.5388	.5152	.4928
	− 90°	.....	.5657	.5393	.5153	.4931
	−120°	.....	.5656	.5394	.5152	.4932
	−150°	.5956	.5667	.5403	.5166	.4941
	−180°	.5966	.5679	.5411	.5171	.4951
1/1500 normal solution.	− 30°	.....	.5612	.5378	.5147	.4938
	− 60°	.....	.5612	.5368	.5149	.4938
	− 90°	.....	.5624	.5373	.5149	.4936
	−120°	.....	.5630	.5382	.5152	.4931
	−150°	.....	.5643	.5382	.5152	.4931
	−180°	.....	.5650	.5385	.5153	.4938
1/15000 normal solution.	− 60°	.....	.5483	.5257	.5038	.....
	− 90°	.....	.5464	.5338	.5027	.4831
	−120°	.....	.5456	.5233	.5021	.4829
	−150°	.....	.5465	.5234	.5020	.4829
	−180°	.....	.5476	.5235	.5021	.4828

The frequency interval, as may be seen from table 113, suffers a marked change with dilution. The 1/15 and 1/150 normal solutions show spectral series of 86.8 and 85.5 average interval respectively, the 1/1500 series of 83.4 units, the 1/15,000 series of only 80.2 units. The 1/1500 series undergo marked increase of interval on cooling.

The bands of the 1/15,000 normal are so greatly shifted that they lie approximately in the middle of the intervals between the bands of the 1/1500 normal solution. Such a "shift" of the entire spectrum must be due to a marked change in the molecular arrangement; hence it can hardly be designated as a shift of the 1/1500 normal spectrum. Presumably a new hydrate has been formed by the freezing of the 1/15,000 normal solution.

The 1/150,000 normal solution gave a spectrum which was too dim to permit of measurement, except at the lowest temperatures. From the three bands which are visible, it appears that the frequency interval

is approximately 77 units. If so, it is the shortest frequency interval yet discovered in the fluorescence of the uranyl salts.

A comparison of the location of the bands of the solid potassium sulphate with those of the 1/15 normal solution shows that the bands of the solutions are from 12 to 40 Å.U. nearer the red, according to their wave-lengths.

URANYL POTASSIUM SULPHATE IN SULPHURIC ACID.

The addition of sulphuric acid in moderate proportions to the aqueous solutions of the potassium sulphate increases the intensity and improves the resolution of the bands.

A solution of the 5 c.c. of 4/15 normal aqueous solution to 1 c.c. of acid was subjected to the cooling process. In figures 92 and 93 and table 114 the shifts will be observed. Band 5, which is typical of the other bands, shifted toward the violet by 21 Å.U. at $-120°$, and then shifted 6 Å.U. toward the red at $-180°$.

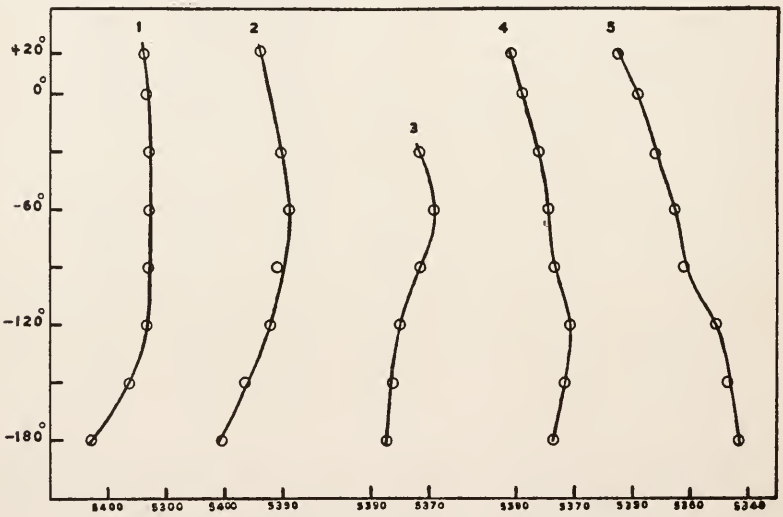

FIG. 92.—Uranyl potassium sulphate—Temperature shift.

(1) 1/15 normal, aqueous; (2) 1/150 normal, aqueous; (3) 1/1500 normal, aqueous; (4) 5 c.c. of 4/15 normal, aqueous to 1 c.c. sulphuric acid; (5) 1 c.c. of 4/15 normal, aqueous to 1 c.c. sulphuric acid.

The addition of acid in larger proportion—1 c.c. of acid to 1 c.c. of 4/15 normal solution—resulted in a spectrum which shifted toward the violet in a peculiar fashion with each decrement of temperature. (See curve No. 5 of fig. 92.) The total shift of band 5 amounted to 42 Å.U.

Further dilution with acid, *e. g.*, 20 c.c. of acid to 1 c.c. of solution, resulted in another broad-banded spectrum at $+20°$. With cooling, however, partial resolution occurred. This is best observed in figure 94, where several narrow bands appear in the regions formerly occupied by the broad bands. Homologous components are lettered *a*, *b*, and *c*.

Still greater dilution—50 c.c. of acid to 1 c.c. of aqueous solution—produced a spectrum which passed through the same development;

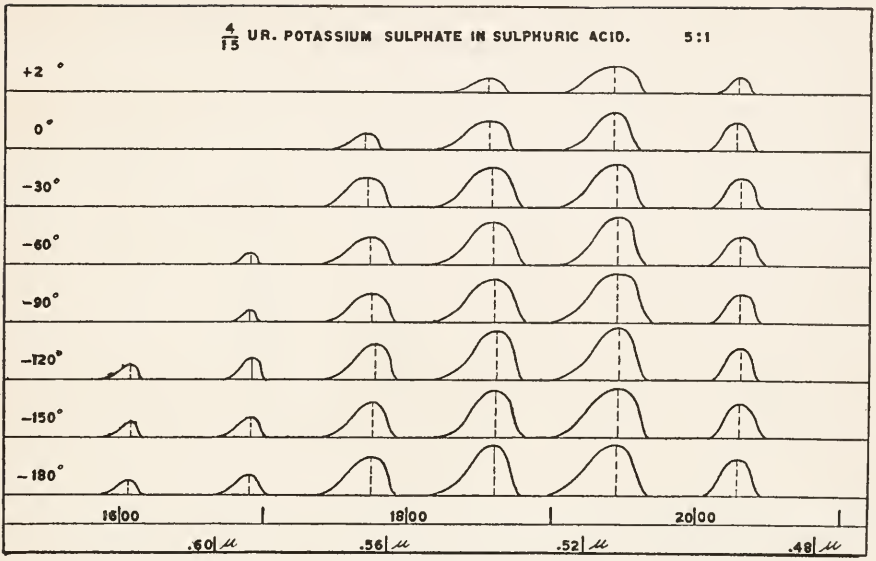

FIG. 93.

TABLE 113.—*Uranyl potassium sulphate in water.—Frequencies and average intervals of fluorescence bands.*

Band.		+20°	0°	−30°	−60°	−90°	−120°	−150°	−180°
Frequencies in 1/15 normal solution.	3	.....	.....	1682.9	1682.1	1682.1	1681.8	1679.8	1676.2
	4	1768.0	1769.6	1769.9	1769.3	1769.0	1769.0	1769.0	1764.0
	5	1856.0	1856.3	1856.7	1856.7	1856.6	1856.3	1854.3	1849.8
	6	1940.2	1941.0	1942.5	1942.5	1942.5	1942.1	1940.2	1935.7
	7	2027.6	2029.2	2030.0	2029.6	2030.0	2029.2	2027.2	2022.2
Average int..		86.5	86.5	86.8	86.9	87.0	86.9	86.9	86.5
Frequencies in 1/150 normal solution.	3	.....	.....	.....	.....	.....	.....	1679.0	1676.1
	4	.....	.....	1767.1	1767.7	1767.7	1768.0	1764.6	1760.9
	5	1852.5	.....	1854.9	1856.0	1854.6	1853.9	1850.8	1848.1
	6	1939.9	.....	1940.6	1941.0	1940.0	1941.0	1935.7	1933.9
	7	.....	.....	2028.0	2029.2	2028.0	2027.6	2023.9	2019.8
Average int..		87.4	.....	87.0	87.2	86.8	86.5	86.2	85.9
Frequencies in 1/1500 normal solution.	4	.....	.....	1781.9	1781.9	1778.1	1776.1	1772.1	1769.9
	5	.....	.....	1860.1	1862.9	1861.2	1858.0	1858.0	1857.0
	6	.....	.....	1942.9	1942.1	1942.1	1941.0	1941.0	1940.6
	7	.....	.....	2025.1	2025.1	2025.9	2028.0	2028.0	2025.1
Average int..		.....	.....	81.1	81.1	82.6	84.0	85.3	85.1
Frequencies in 1/15000 normal solution.	4	.....	.....	.....	1823.8	1830.2	1832.8	1829.8	1826.2
	5	.....	.....	.....	1902.2	1909.1	1911.0	1910.6	1910.2
	6	.....	.....	.....	1984.9	1989.3	1991.6	1992.0	1991.6
	7	.....	.....	.....	.....	2070.8	2070.8	2070.8	2071.3
Average int..		.....	.....	.....	80.6	79.3	79.3	80.3	81.7

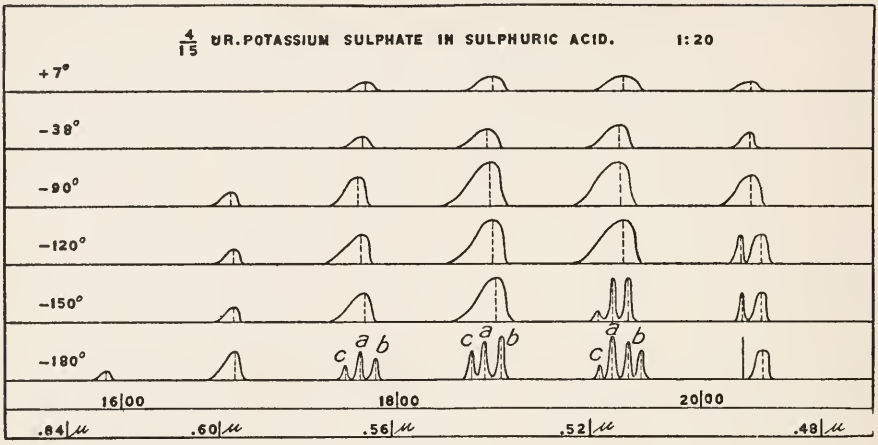

FIG. 94.

hence it is clear that the presence of sulphuric acid in excess is essential to resolution of this type.

The homologous components formed frequency intervals which were constant and of the same length as those of the parent bands; *i. e.*, the homologous components form separate series.

TABLE 114.—*Uranyl potassium sulphate in sulphuric acid.*

Temp., etc.		Band 2.	Band 3.	Band 4.	Band 5.	Band 6.	Band 7.
5 c.c. of 4/15 normal aqueous solution with 1 c.c. of acid.	+ 20°	.....	.....	.....	0.5392	0.5150	0.4931
	0°	.....	.....	0.5650	.5388	.5150	.4933
	− 30°	.....	.....	.5642	.5382	.5145	.4927
	− 60°	.....	0.5917	.5638	.5379	.5142	.4928
	− 90°	.....	.5917	.5635	.5377	.5142	.4926
	−120°	0.6219	.5911	.5625	.5371	.5136	.4921
	−150°	.6220	.5914	.5631	.5373	.5139	.4926
	−180°	.6226	.5917	.5633	.5377	.5141	.4928
1 c.c. of 4/15 normal aqueous solution with 1 c.c. of acid.	+ 20°	.....	.....	.5650	.5385	.5141	.4921
	− 2°	.....	.5946	.5647	.5378	.5142	.4918
	− 35°	.....	.5938	.5635	.5374	.5136	.4916
	− 63°	.6230	.5921	.5629	.5364	.5131	.4911
	− 90°	.6227	.5915	.5621	.5362	.5127	.4908
	−120°	.6211	.5903	.5611	.5350	.5117	.4898
	−150°	.6203	.5887	.5603	.5347	.5113	.4896
	−180°	.6194	.5885	.5600	.5343	.5107	.4892

Temp., etc.		Band 3.	Band 4*a*.	Band 5*a*.	Band 5*b*.	Band 6*a*.	Band 6*b*.	Band 7*a*.	Band 7*b*.
1 c.c. of 4/15 normal aqueous solution with 50 c.c. acid.	0°	.....	0.5662	.....	0.5388	.....	0.5138	.....	0.4914
	− 30°	.....	.5666	.....	.5394	.....	.5146	.....	.4916
	− 60°	0.5966	.5662	.....	.5388	.....	.5141	.....	.4911
	− 90°	.5966	.5661	.....	.5387	.....	.5140	.....	.4905
	−120°	.5968	.5659	.....	.5385	.....	.5139	.....	.4902
	−150°	.5979	.5663	.....	.5380	0.5158	.5119	0.4930	.4897
	−180°	.5942	.5634	0.5401	.5376	.5151	.5118	.4928	.4895

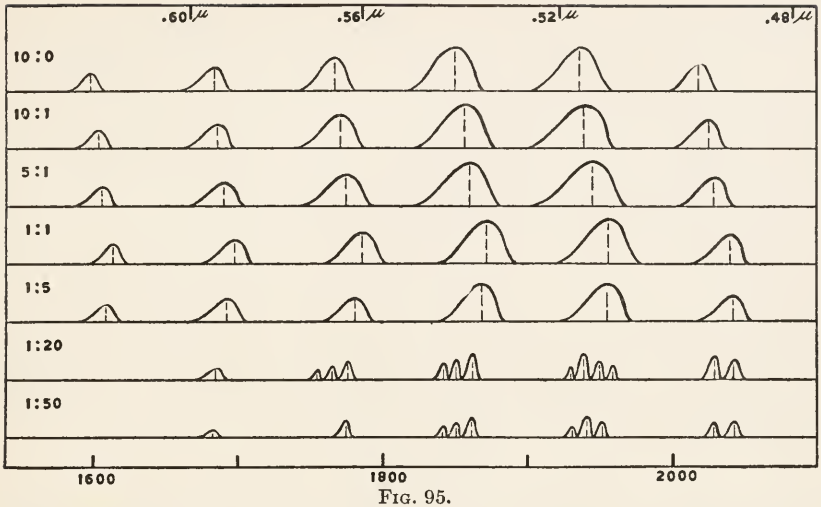

FIG. 95.

TABLE 115.—*Uranyl potassium sulphate in sulphuric acid.—Frequencies and average intervals of fluorescence bands.*

Band, etc.		+20°	0°	−30°	−60°	−90°	−120°	−150°	−180°
Frequencies of 5 c.c. 4/15 normal aqueous with 1 c.c. acid.	2	.....	.....	.....	.....	.....	1608.0	1607.7	1606.2
	3	.....	.....	.....	1690.0	1690.0	1691.8	1690.9	1690.0
	4	.....	1769.9	1772.4	1773.7	1774.6	1777.8	1775.9	1775.3
	5	1854.6	1856.0	1858.0	1859.1	1859.8	1861.9	1861.2	1859.8
	6	1941.7	1941.7	1943.6	1944.8	1944.8	1947.0	1945.9	1945.1
	7	2028.0	2027.2	2029.6	2029.2	2030.0	2032.1	2030.0	2029.2
Av. int.....		86.7	85.8	85.7	84.8	84.8	84.8	84.5	84.6

Band, etc.		+20°	−2°	−35°	−63°	−90°	−120°	−150°	−183°
Frequencies of 1 c.c. 4/15 normal aqueous with 1 c.c. acid.	2	.....	.....	.....	1605.1	1605.9	1610.0	1612.1	1614.5
	3	.....	1681.8	1684.1	1688.9	1690.6	1694.1	1698.7	1699.2
	4	1769.9	1770.9	1774.6	1776.5	1779.0	1782.2	1784.8	1785.7
	5	1857.0	1859.4	1860.8	1864.3	1865.0	1869.2	1870.2	1871.6
	6	1945.1	1944.8	1947.0	1948.9	1950.5	1954.3	1955.8	1958.1
	7	2032.1	2033.3	2034.2	2036.2	2037.5	2041.7	2042.5	2044.2
Av. int.....		87.4	87.9	87.5	86.2	86.3	86.3	86.1	85.9

Band, etc.		+20°	0°	−30°	−60°	−90°	−120°	−150°	−180°
Frequencies of 1 c.c. 4/15 normal aqueous with 50 c.c. acid.	3	.....	.....	.....	1676.2	1676.2	1675.6	1672.5	1682.9
	4*a*	.....	1766.2	1764.9	1766.2	1766.5	1767.1	1765.8	1774.9
	5*a*	.....	.....	.....	.....	.....	.....	.....	1851.5
	5*b*	.....	1856.0	1853.9	1856.0	1856.3	1857.0	1858.7	1860.1
	6*a*	.....	.....	.....	.....	.....	.....	1938.7	1941.4
	6*b*	.....	1946.3	1943.3	1945.1	1945.5	1945.9	1953.5	1953.9
	7*a*	.....	.....	.....	.....	.....	.....	2028.4	2029.2
	7*b*	.....	2035.0	2034.2	2036.2	2038.7	2040.0	2042.1	2042.9
Av. int.....		.....	89.6	89.8	90.0	90.6	91.1	92.4	90.0

The effect of dilution with acid at one temperature is given in table 115. The −180° spectra of the 4/15 normal aqueous solution with varying proportions of acid are shown in figure 95. With the addition of acid the bands at first move toward the violet without resolving, then become stationary in position, and finally resolve. The ratio by volume of aqueous solution to sulphuric acid is given for each spectrum. The shift is not the same for the different bands, because the frequency interval, beginning with about 85 units for the aqueous solution, increases with increase of acid component to about 90 units in the 50 parts acid to 1 part water solution. With the exception of the two resolved spectra, the bands are too diffuse to permit of satisfactory intermediate measurements on the frequency intervals. Dilution with acid has undoubtedly *increased* the interval by 5 units, whereas dilution with water *decreased* the interval by 8 units.

URANYL CHLORIDE IN WATER.

The absorption spectrum of the chloride is of particular interest, since Jones and Strong first located absorption bands[1] in the fluorescence region in an aqueous solution of this salt. Observations by the authors on the transmission spectrum of several crystals of the uranyl double chlorides of potassium, ammonium, rubidium, and cæsium have

TABLE 116.—*Uranyl chloride in water.*

Solution and temp.	Band 2.	Band 3.	Band 4.	Band 5.	Band 6.	Band 7.
3.0 normal solution. −97°	0.6247	0.5935	0.5639	0.5383	0.5142	0.4927
3.0 normal solution. −120°	.6250	.5940	.5644	.5379	.5140	.4925
3.0 normal solution. −150°	.6254	.5939	.5644	.5379	.5139	.4925
3.0 normal solution. −180°	.6255	.5939	.5645	.5386	.5143	.4926
1.5 normal solution. −90°	.6245	.5931	.5643	.5382	.5141	.4926
1.5 normal solution. −120°	.6246	.5935	.5643	.5382	.5142	.4929
1.5 normal solution. −150°	.6252	.5936	.5643	.5382	.5141	.4926
1.5 normal solution. −180°	.6252	.5934	.5642	.5382	.5141	.4926
0.5 normal solution. −90°	.6236	.5938	.5648	.5385	.5146	.4926
0.5 normal solution. −120°	.6249	.5936	.5646	.5386	.5144	.4923
0.5 normal solution. −150°	.6251	.5933	.5646	.5385	.5143	.4924
0.5 normal solution. −180°	.6254	.5936	.5645	.5382	.5144	.4926
0.05 normal solution. −90°	.....	.5941	.5645	.5382	.5144	.4923
0.05 normal solution. −120°	.6253	.5942	.5647	.5381	.5141	.4923
0.05 normal solution. −150°	.6254	.5939	.5649	.5381	.5142	.4923
0.05 normal solution. −180°	.6252	.5935	.5646	.5382	.5144	.4924

resulted in the discovery of absorption bands in the same region. The view held by Jones that the fluorescence spectrum is a continuation of the absorption spectrum is to be gravely doubted, for while the chloride solution shows a fluorescence band at 0.4926 and Jones has established the position of an absorption band at 0.4920, none of the other bands

[1] Jones and Strong. Carnegie Inst. Wash. Pub. No. 130, p. 90.

located by him at 0.6070, 0.6040, 0.6020, 0.6000. 0.5200, or 0.5185 coincide with a band of the fluorescence spectrum. Furthermore, it has previously been indicated that often the last band of a fluorescence spectrum coincides fairly well with a strong band in the absorption. It has also been shown in our study of the fluorescence and absorption spectra of the crystalline salts (see Chapters III to IX) that the interval between the absorption bands, although constant, is much smaller than that between fluorescence bands.

The bands of the chloride in solution are separated by a very black background, but are so dim that cooling to −90° is necessary before measurements can be made. The bands continue to increase in brightness as the temperature is further decreased.

The temperature shift between −90° and −180° is toward the red in the spectrum of the 3.0 normal solution. The measurements on the chloride, to be found in tables 116 and 117, indicate that difficulty is experienced in locating the positions of the bands. The remarkable

TABLE 117.—*Uranyl chloride in water—Frequencies and average intervals, fluorescence bands.*

Band.		−97°	−120°	−150°	−180°
Frequencies in 3.0 normal solution.	2	1600.8	1600.0	1599.0	1598.7
	3	1684.9	1683.5	1683.8	1683.8
	4	1773.4	1771.8	1771.8	1771.5
	5	1857.7	1859.1	1859.1	1856.7
	6	1944.8	1945.5	1945.9	1944.4
	7	2029.6	2030.5	2030.5	2030.0
Av. int.....		85.8	86.1	86.3	86.3
Frequencies in 1.5 normal solution.	2	1601.3	1601.0	1599.5	1599.5
	3	1686.1	1684.9	1684.6	1685.2
	4	1772.1	1772.1	1772.1	1772.4
	5	1858.0	1858.0	1858.0	1858.0
	6	1945.1	1944.8	1945.1	1945.1
	7	2030.0	2028.8	2030.0	2030.0
Av. int.....		85.7	85.6	86.1	86.1
Frequencies in 0.5 normal solution.	2	1603.6	1600.3	1599.7	1599.0
	3	1684.1	1681.8	1685.4	1584.6
	4	1770.5	1771.2	1771.2	1771.5
	5	1857.0	1856.7	1857.0	1858.0
	6	1943.3	1944.0	1944.4	1944.0
	7	2030.0	2031.3	2030.9	2030.0
Av. int.....		86.3	86.2	86.2	86.2
Frequencies in 0.05 normal solution.	2	.....	1599.2	1599.0	1599.5
	3	1683.2	1682.9	1683.8	1684.9
	4	1771.5	1770.9	1770.2	1771.2
	5	1858.0	1858.4	1858.4	1858.0
	6	1944.0	1945.1	1944.8	1944.0
	7	2031.3	2031.3	2031.3	2030.9
Av. int.....		87.0	86.4	86.5	86.3

fact is that the bands of the 1.5, 0.5, and 0.05 normal solutions are not shifted by temperature, and that dilution from 3.0 normal to 0.05 normal produces a negligible shift. There is no tendency toward resolution. Clearly, the uranyl chloride in aqueous solution furnishes spectra of great stability, especially in view of the behavior of the bands of the uranyl nitrate.

URANYL NITRATE IN WATER.

The solutions of uranyl nitrate present at once the most interesting and most complicated spectra. In our first investigations the solutions were studied at $-185°$ after suddenly plunging them into liquid air. Later it became of interest to study them at several intermediate

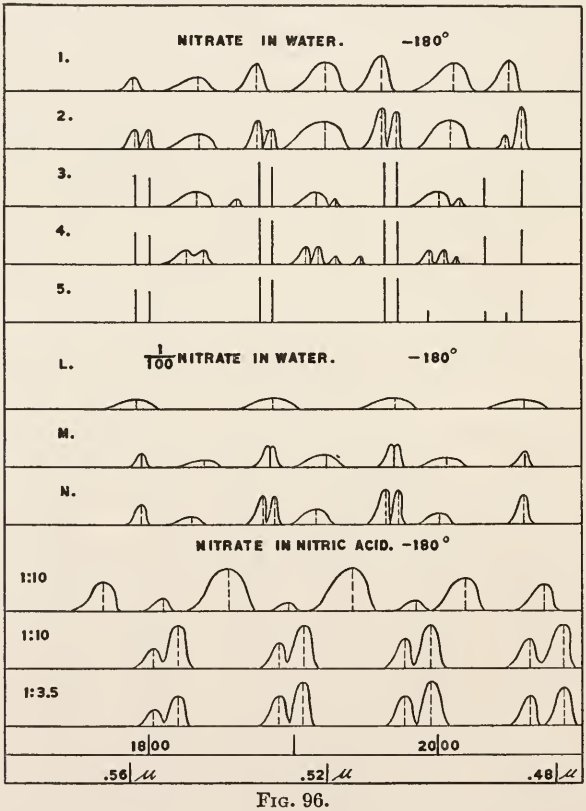

FIG. 96.

temperatures and the freezing and subsequent cooling was of necessity done slowly. To our surprise, the normal solution of the nitrate yielded an entirely different type of spectrum. Spectrum No. 1 at the top of figure 96 represents the old type and spectrum No. 5 the new type. It was found possible to produce intermediate degrees of resolution somewhat similar to Nos. 2, 3, and 4 by intermediate rates of cooling. The pertinent fact is that the identical solution could, by

manipulation of the cooling process, be made to yield either an unresolved or a highly resolved spectrum. The intermediate forms were not easy to reproduce at will. A comparison of the wave-lengths of the strongly resolved bands of the solution at −180° with those of the crystalline salt at the same temperature *showed that they were identical.*

The uranyl ammonium nitrate and uranyl potassium nitrate in aqueous solution were similarly cooled and showed resolution of the same type. Resolution of this type has not been discovered in any other aqueous solutions, but in our first investigation uranyl acetate in alcohol was found to give highly resolved but quite dim bands superimposed on a continuous background. The spectra of the 1/100 normal solution were similarly affected by retarding the rate of cooling. Spectra L, M, and N of figure 96 show the results of successively slower rates of cooling.

EFFECT OF TEMPERATURE ON SLOWLY COOLED SOLUTIONS OF URANYL NITRATE.

Since the changes in the spectrum of the normal solution are very striking and are typical of the changes in many other more dilute solutions, a detailed account of the changes in this spectrum is given. Figure 97 gives a plot of the spectra. Some attempt at indicating the

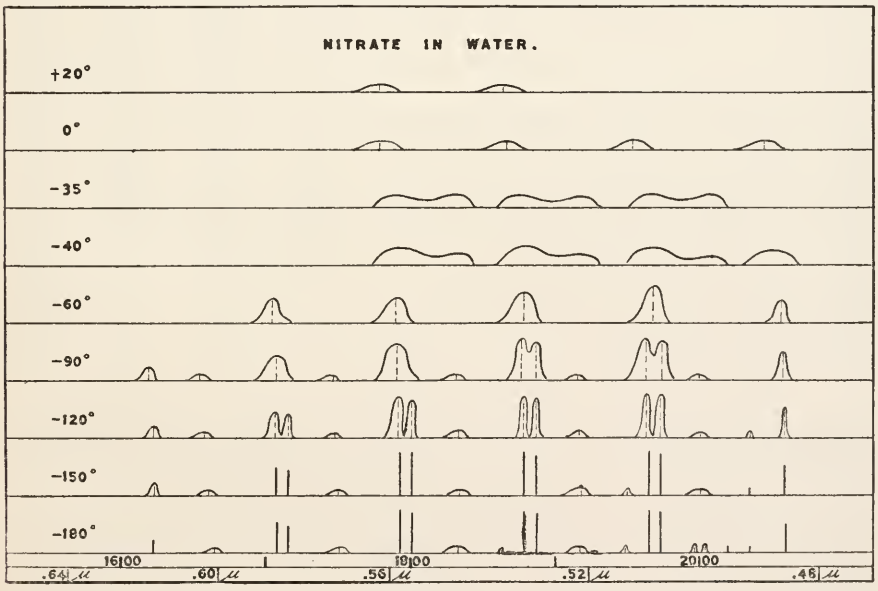

FIG. 97.

form of the bands is made, but the changes in intensity are too great to be represented on such a plot. The wave-lengths are tabulated in table 118, and frequencies in table 119. At +20° only two broad bands located at 0.5323 and 0.5088 were of sufficient intensity to be measur-

able. With falling temperature these increased in brightness and two more bands came up to the threshold of vision. Bands 0.4890 at 0° corresponds with an absorption band at 0.4870 discovered by Jones and Strong. The crystalline nitrate, with 6 H_2O, also has an absorption band at 0.4870.

While continuing the cooling process at a slow rate, a sharp rise in temperature from −25° to −18° was invariably noticed, probably due to undercooling or change in hydration. Immediately following this stage portions of the background increased greatly in brightness so as to broaden each band on the violet side. These very broad bands, which exist at temperatures between −25° and −40°, were found on subsequent cooling to be the parents of groups of resolved bands. The −40° bands were five times the intensity of the +20° bands.

TABLE 118.—*Uranyl nitrate in water—normal solution.*

	Temperature.							
	+20°	0°	−40°	−60°	−90°	−120°	−150°	−180°
Strong..	.....	.....	.....	0.6175	0.6174	0.6161	0.6183	0.6165
Weak...	.....	.....	.....	.....	.6039	.6030	.6022	.6006
Strong..	.....	.....	0.5932–0.5696	.5864	.5855	.5857	.5861	.5857
Weak...	.....	.....	.....	.....	.....	.5829	.5827	.5823
Dim....	.....	.....	.....	.....	.5723	.5722	.5713	.5712
Strong..	.....	0.5622	.....	.5582	.5584	.5579	.5577	.5576
Dim....	.....	.....	.....	.....	.....	.5553	.5554	.5553
Dim....	.....	.....	.....	.....	.5461	.5457	.5454	.5455
Dim....	.....	.....	.....	.....	.....	.....	.....	.5368
Strong..	0.5323	.5350	.5375–0.5182	.5323	.5331	.5322	.5322	.5322
Dim....	.....	.....	.....	.....	.5299	.5300	.5299	.5299
Dim....	.....	.....	.....	.....	.5219	.5216	.5214	.5217
Dim....	.....	.....	.....	.....	.....	.....	.5129	.5132
Strong..	.5088	.5110	.5129–0.4951	.5082	.5093	.5093	.5090	.5089
Dim....	.....	.....	.....	.....	.5065	.5069	.5068	.5068
Dim....	.....	.....	.....	.....	.....	.....	.....	.5008
Dim....	.....	.....	.4924–0.4831	.....	.4999	.4997	.4997	.4991
Dim....	.....	.....	.....	.....	.....	.....	.....	.4951
Dim....	.....	.....	.....	.....	.....	.4914	.4916	.4914
Strong..	.....	.4890	.....	.4862	.4858	.4857	.4856	.4855

At −46° the portion of each band toward the violet decreased in intensity as the part of longer wave-length became stronger, thereby tending to both narrow the band and produce a decided crest. It was found, with the aid of the spectro-photometer, that the intensity of the stronger crest at −60° was 85 times that of the homologous band at +20°.

Further cooling resolved the stronger band into doublets without a real shift, but the dimmer component was not so easily resolved. At temperatures between −120° and −180° the strongly resolved doublets formed two series, both of a constant frequency interval of 88 units, the single band at 0.4885 being a member of one series. There was

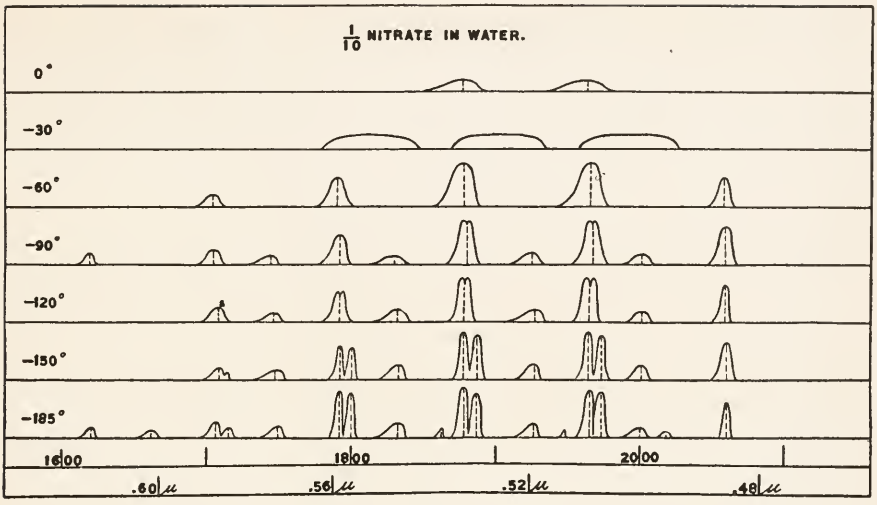

FIG. 98.

no shift here, but increasingly better resolution. The very dim intermediate bands resolved to form series of approximately the same interval.

It was thought that by reversing the cooling process the spectra might go through the same forms at the same temperatures, which

TABLE 119.—*Uranyl nitrate in water—frequencies and average intervals of fluorescence bands.*

Band.	−20°	0°	−40°	−60°	−90°	−120°	−150°	−180°
2	.....	.....	.....	1619.4	1619.7	1623.1	1622.6	1616.8
	.....	.....	.....	.....	1655.9	1658.4	1660.6	1665.0
3	.....	.....	1685.8–1755.6	1705.3	1705.0	1707.4	1706.2	1707.4
	.....	.....	.....	.....	.....	1715.6	1716.1	1717.3
	.....	.....	.....	.....	1747.3	1747.6	1750.4	1750.7
4	.....	1778.7	.....	1791.5	1790.8	1792.4	1793.1	1793.4
	.....	.....	.....	.....	.....	1800.8	1800.5	1800.8
	.....	.....	.....	.....	1831.2	1832.5	1833.5	1833.2
5	.....	.....	.....	.....	.....	.....	.....	1862.9
	1878.6	1869.2	1860.5–1929.8	1878.6	1875.8	1879.0	1879.0	1879.0
	.....	.....	.....	.....	1887.1	1886.8	1887.1	1887.1
	.....	.....	.....	.....	1916.1	1917.2	1917.9	1916.8
6	.....	.....	.....	.....	.....	.....	1949.7	1948.6
	1965.4	1956.9	1949.7–2019.8	1967.7	1963.5	1963.5	1964.6	1965.0
	.....	.....	.....	.....	1974.3	1972.8	1973.2	1973.2
	.....	.....	.....	.....	.....	.....	.....	1996.8
	.....	.....	2030.9–2070.0	.....	2000.4	2001.2	2001.2	2003.6
	.....	.....	.....	.....	.....	.....	.....	2019.9
7	.....	.....	.....	.....	.....	2035.0	2034.1	2035.0
	.....	2045.0	.....	2056.8	2058.5	2058.9	2059.3	2059.7
Av. int.	86.8	88.8	89.8	87.5	87.8	87.2	87.3	88.6

proved to be the case when the temperature was raised from −180° to −60°, but on further heating to −30° the −60° spectrum failed to change over to the very broad banded form. Finally, the temperature was raised to −18°, the cryohydrate point. The original spectrum of the unfrozen solution then reappeared.

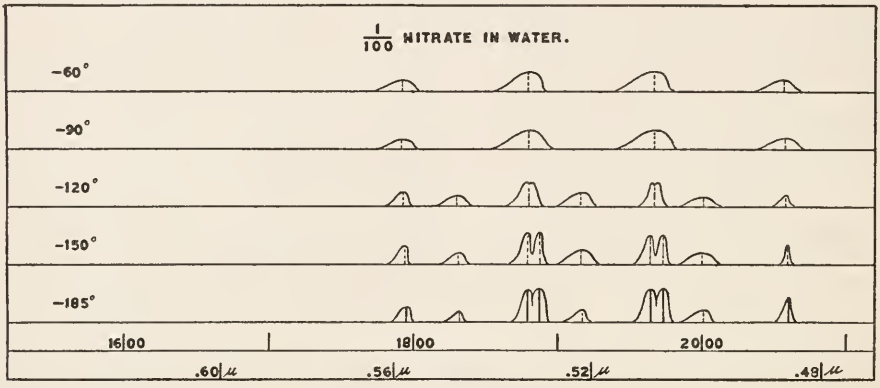

Fig. 99.

The slow cooling of the 1/10 normal solution produced a series of spectra similar to the above, but dimmer and not quite as well defined. (See fig. 98.) The 1/100 normal, although too dim to be measured

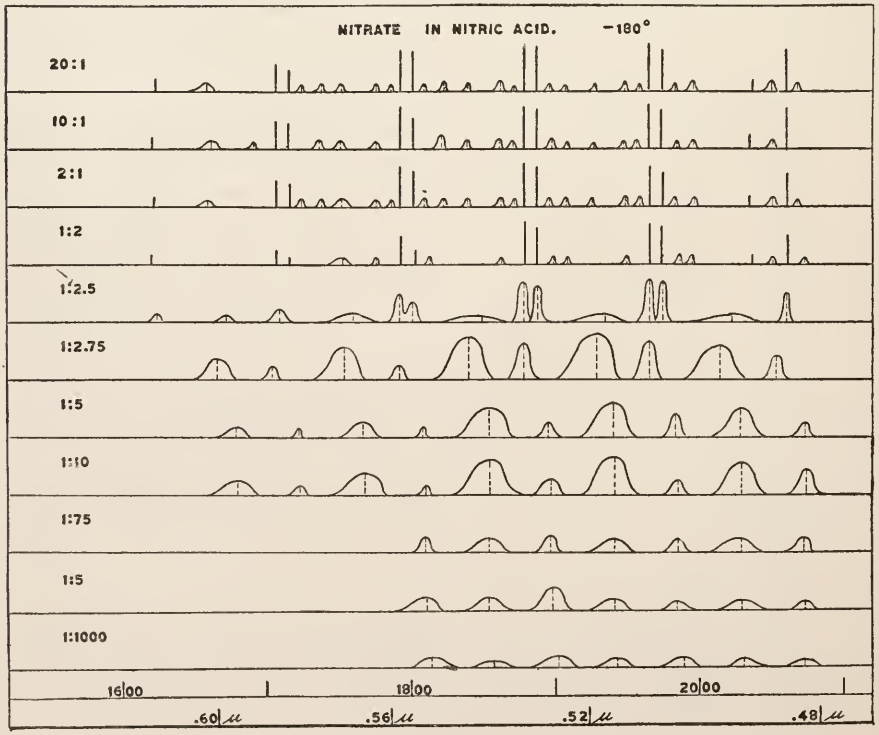

Fig. 100.

until a temperature of −60° was reached, behaved similarly. (See fig. 99.) The more dilute aqueous solutions, *e. g.*, the 1/200 and 1/500 normal, gave broad bands with no important shifts.

The very dim, broad bands of the 1/1000 and 1/10,000 normal are probably due to the production of different hydrates.

URANYL NITRATE IN NITRIC ACID.

The spectra of the normal aqueous solution diluted with nitric acid in varying proportion are shown in figure 100. Data for 5 c.c. of acid are given in tables 120 and 121.

TABLE 120.

Uranyl nitrate in nitric acid (1 c.c. of normal aqueous solution with 5 c.c. of acid).					
−30°	−60°	−90°	−120°	−150°	−180°
.....	.....	.....	.....	0.5958	0.5965
.....	0.5817	0.5810	0.5808	.5818	.5806
.....	.....	.....	.5681	.5673	.5654
0.5540	.5540	.5531	.5528	.5527	.5531
.....	.....	.....	.5412	.5399	.5393
.5289	.5283	.5274	.5274	.5280	.5279
.....	.....	.....	.5165	.5163	.5154
.5064	.5047	.5045	.5042	.5045	.5043
.....	.....	.....	.4941	.4935	.4930
.....	.4832	.4823	.4824	.4825	.4823

Uranyl nitrate in methyl alcohol (0.1 normal solution).				Uranyl nitrate in ethyl alcohol (0.1 normal solution).			
−120°	−135°	−150°	−180°	−90°	−120°	−150°	−180°
.....	.....	.....	0.6045	.....	0.5834	0.5836	.05788
0.5841	0.5894	0.5891	.5882	0.5537	.5557	.5552	.5521
.....	.5804	.5780	.5780	.5287	.5301	.5300	.5270
.5569	.5605	.5602	.5600	.5069	.5072	.5072	.5040
.....	.5525	.5510	.5503	.....	.....	.....	.4889
.5318	.5345	.5344	.5341	.....	.....	.....	.4828
.....	.5272	.5263	.5252				
.5091	.5106	.5108	.5104				
.....	.5041	.5031	.5025				
.4887	.4887	.4888	.4887				
.....	.....	.4819	.4815				

The uppermost spectrum, denoted at the left by 20 : 1, was produced by slowly cooling to −180° and exciting to luminescence a solution of 20 c.c. of the normal aqueous solution mixed with 1 c.c. of acid. The first effect of the acid was to bring out more distinctly the dimmest bands of the aqueous solution. There was no marked shift or change in resolution as the acid component was increased until the solution contained 1 c.c. of normal aqueous solution to 2 c.c. of acid. With further dilution, *e. g.*, 1 c.c. of solution to 2.75 c.c. of acid, a marked change in the spectrum occurred, for only a broad-banded series of

TABLE 121.—*Uranyl nitrate in nitric acid—Frequencies and average intervals of fluorescence bands.*

Frequencies in 1 c.c. of normal aqueous with 5 c.c. of acid.							
Band.	−30°	−60°	−90°	−120°	−150°	−180°	
2	.....	.....	.....	.....	1678.4	1676.4	.....
3	.....	1719.1	1721.2	1721.8	1718.8	1722.4	.....
	.....	.....	.....	1760.3	1762.7	1768.6	.....
4	1805.1	1805.1	1808.0	1809.0	1809.3	1808.0	.....
	.....	.....	.....	1847.7	1852.2	1854.3	.....
5	1890.7	1892.9	1896.1	1896.1	1893.9	1894.3	.....
	.....	.....	.....	1936.1	1936.9	1940.4	.....
6	1974.7	1981.4	1982.2	1983.3	1982.2	1982.2	.....
	.....	.....	.....	2023.9	2026.3	2028.4	.....
7	.....	2069.5	2073.4	2073.0	2072.5	2073.4	.....
Av. int.	84.8	87.6	88.1	87.8	88.4	87.8	.....

Uranyl nitrate in methyl alcohol—Frequencies in 0.1 c.c. normal solution in alcohol.							
Band.	−30°	−60°	−90°	−120°	−135°	−150°	−180°
2	.....	.....	.....	.....	.....	.....	1654.3
3	.....	.....	.....	1712.0	1966.6	1697.5	1700.1
	.....	.....	.....	.....	1723.0	1730.1	1730.1
4	.....	.....	.....	1795.7	1784.1	1785.1	1785.7
	.....	.....	.....	.....	1810.0	1814.9	1817.2
5	.....	.....	.....	1880.4	1870.9	1871.3	1872.3
	.....	.....	.....	.....	1896.8	1900.1	1904.0
6	.....	.....	.....	1964.3	1958.5	1957.7	1959.2
	.....	.....	.....	.....	1983.7	1987.7	1990.1
7	.....	.....	.....	2046.2	2046.2	2045.8	2046.2
	.....	.....	.....	.....	.....	2075.1	2076.8
Av. int.	.....	.....	.....	83.6	87.4	87.1	86.8

Uranyl nitrate in ethyl alcohol—Frequencies in 0.1 c.c. normal solution in alcohol.							
Band.				−90°	−120°	−150°	−180°
3	.....	.....	.....	.....	1714.1	1713.5	1727.7
4	.....	.....	.....	1806.0	1799.5	1801.2	1811.3
5	.....	.....	.....	1891.4	1886.4	1886.8	1897.5
6	.....	.....	.....	1972.8	1971.7	1971.6	1984.1
7	.....	.....	.....	.....	.....	.....	2045.5
	.....	.....	.....	.....	.....	.....	2071.3
Av. int.	.....	.....	.....	83.4	85.8	86.1	85.9

doublets is present. This is probably caused by a change in the hydrate at this dilution. This type of spectrum persisted through five more dilute solutions, even when the solution contained only 1 part aqueous solution to 1,000 parts acid.

The effect of slowly cooling five of the acid solutions is seen in figures 101, 102, 103, 104, and 105.

Very often combinations of acid and aqueous solution proved to be unstable on freezing; consequently it was difficult to reproduce at

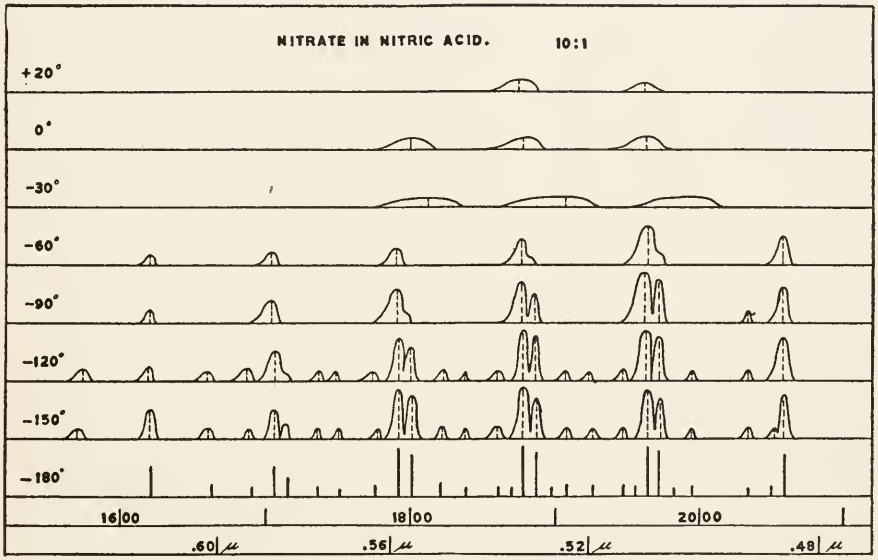

FIG. 101.

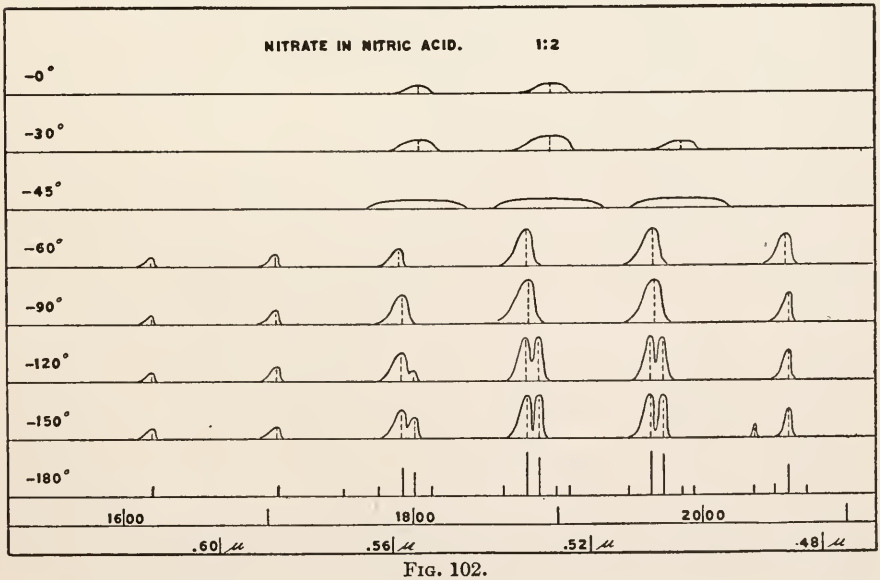

FIG. 102.

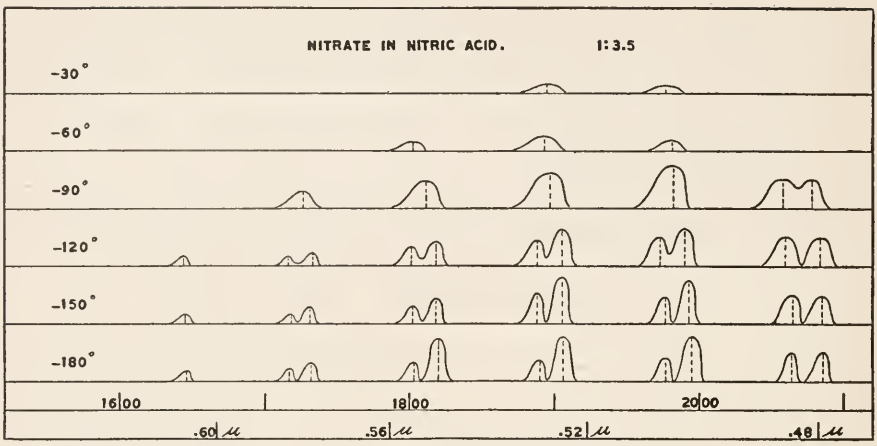

FIG. 103.

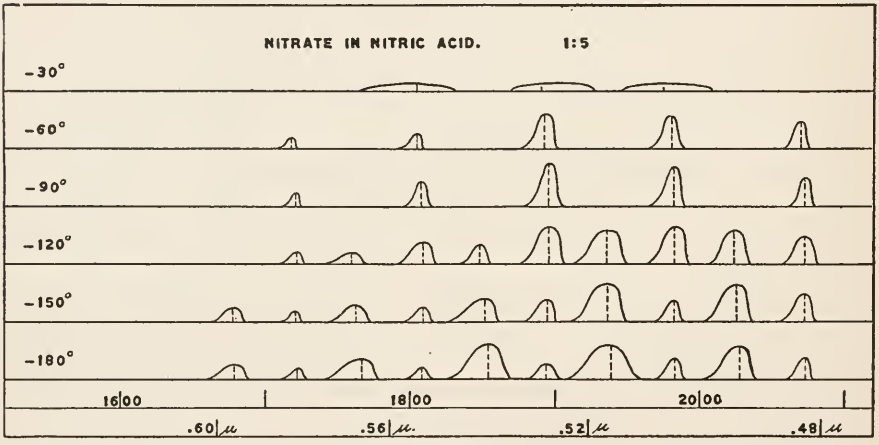

FIG. 104.

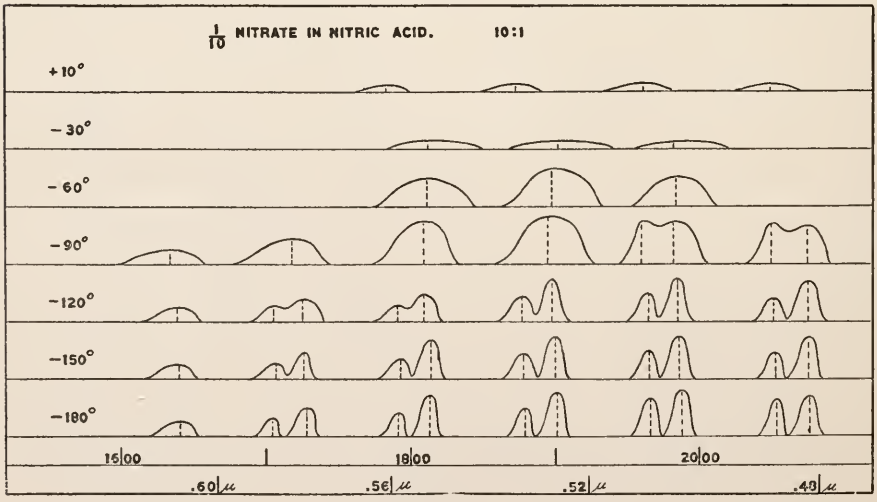

FIG. 105.

will the spectra of such solutions. This appeared to be somewhat independent of the rate of cooling; thus, it was discovered that a solution might yield a spectrum consisting of a set of broad-banded doublets at one time and a narrower set of doublets differently spaced at other times. The three spectra shown at the bottom of figure 96 illustrate this phenomenon. The first two spectra, although entirely different, were produced from a solution of 1 part normal aqueous solution with 10 parts nitric acid. The first was obtained after very slow cooling, the second after moderately slow cooling to liquid air. The second spectrum is identical with the third, obtained by slowly cooling a solution of 1 c.c. of normal solution to 3.5 c.c. of nitric acid. Such experiments lead to the view that the luminescence spectrum is determined by the particular hydrate which is formed on freezing.

The frequency interval of an acid or aqueous solution was always constant. The change in interval through a wide range of dilutions was slight. The largest interval was of 87+, the smallest of 84+ units.

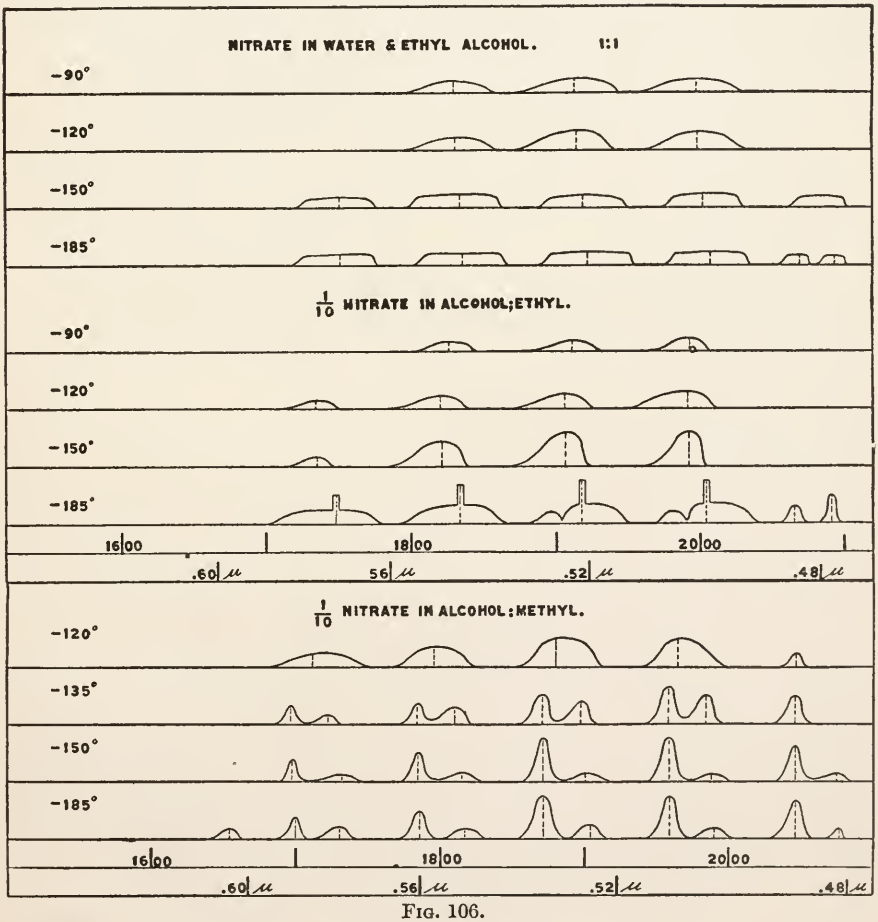

FIG. 106.

THE URANYL NITRATE IN ALCOHOL.

The luminescence spectrum of the normal aqueous solution diluted with ethyl alcohol is distinctly different from that of the aqeous solution. (See fig. 106.) The sharply resolved spectrum is quenched and the new bands are not in the same positions. The unfrozen solutions in a mixture of alcohol and water are not so opaque as the aqueous solutions; hence it is necessary to freeze them to produce sufficient absorption to bring out the luminescence. The first readings were taken when the temperature was $-90°$, and a consistent shift to the violet was effected by further reduction in temperature.

The spectrum of a solution of uranyl-nitrate crystals in ethyl alcohol will also be found in figure 106. At $-90°$, $-120°$, and $-150°$ slight change in form or wave-length occurs, but at $-185°$ fairly well resolved, crests protrude above the crests of the broad bands, still existent. It is probable that one series is due to the water of crystallization, the other to the alcohol. Jones and Strong[1] have attributed the presence of two sets of absorption bands in the water and alcohol solutions to the presence of both a hydrate and an alcoholate, and the two luminescence spectra are undoubtedly caused by such a combination.

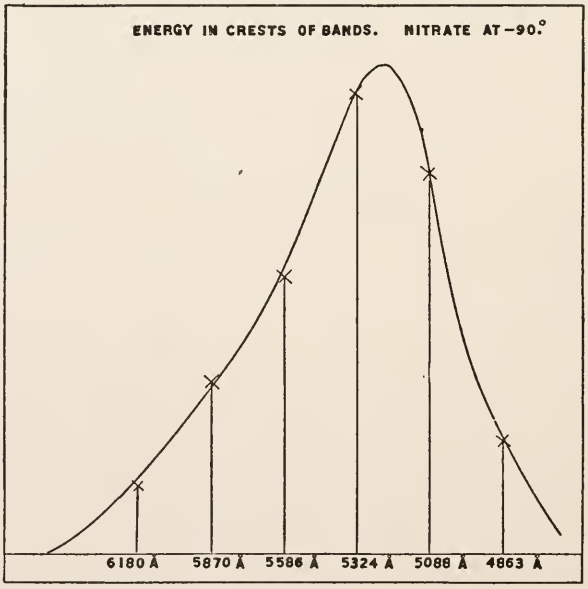

FIG. 107.

A solution of uranyl nitrate in methyl alcohol (fig. 106) presented bands which in the manner of development with temperature resembled the aqueous bands. The doublets fall into two series of constant intervals. It will be observed in figure 106 that the bands of the alcoholic solutions are in approximately the same positions.

[1] Loc. cit., p. 104.

ENERGY DISTRIBUTION IN THE BANDS OF URANYL NITRATE.

The normal aqueous solution at $-90°$ was studied with the aid of the spectrophotometer and bar, the intensity of the crests of the bands being matched by the intensity of the acetylene flame at the same wave-length. These values were multiplied by the ordinates of the corresponding wave-lengths of the energy curve for acetylene.[1] Figure 107 shows the manner in which the bands differed in intensity. The envelope is of the same form as that determined by Nichols and Merritt[2] for the individual bands of the crystalline salts.

SUMMARY OF CHANGES.

The changes produced by slowly changing the temperature from $+20°$ to $-180°$ include:

(1) An increase in intensity of the entire spectrum.
(2) A shift which is more often toward the violet than toward the red, although both shifts may occur between the above temperatures.
(3) A narrowing of the bands and in some solutions a resolution of the bands.
(4) A slight change in the frequency interval.
(5) The formation of one or more definite hydrates.
(6) A change in the form of the bands.

The changes produced by dilution include:

(1) A shift of the entire spectrum.
(2) A change of interval.
(3) A change in the hydrate.
(4) A decrease in the resolution, excepting when small amounts of acid are added to an aqueous solution.
(5) A decrease in intensity.

CONCLUSIONS.

(1) The constant-frequency intervals are due to the uranium oxide.

(2) The small shifts are due to a change in the relative intensity of two or more components of a band.

(3) The more remarkable changes in position are caused by the presence of a new hydrate.

(4) The change in hydrate is probably often associated with a change in the crystal system, and when this phenomenon occurs a change in the grouping of the component bands occurs. The work on four double nitrates[3] (Chapter VII) indicates that the crystal system is an important factor in the determination of the positions of the bands.

(5) The invariable production of broad bands with extensive aqueous dilution is due to complete ionization.

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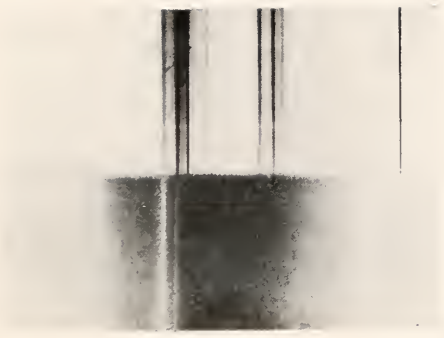
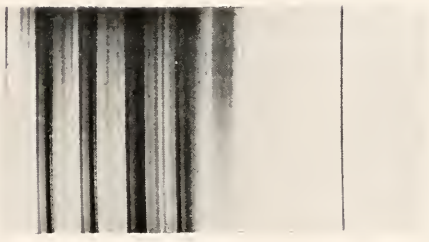
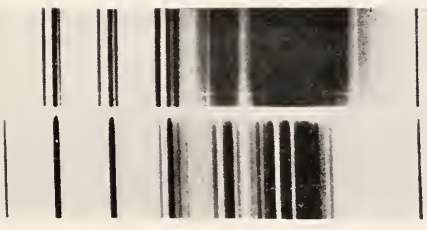
[1] Coblentz. Bureau of Standards, v. 7, No. 2, p. 259.
[2] Nichols and Merritt. Physical Review (1), 32, p. 358.
[3] Howes and Wilber. Physical Review (2), xi, p. 66. 1918.



A



B



C

(*A*) A double reversal in uranyl sulphate at 185° C.
(*B*) The fluorescence of uranyl ammonium nitrate at 185° C.
(*C*) The polarized fluorescence and absorption of uranyl cæsium chloride at 185° C.
Photographic reproductions from the original spectrographs by Dr. R. C. Rodgers

APPENDIX 1.

CHEMISTRY OF FLUORESCING URANYL SALTS.

The compounds studied in this work were those uranyl compounds which showed a bright fluorescence. These in general were salts of the stronger acids and usually double salts with the alkali metals. The further general characteristics were high solubility and much water of crystallization, *i. e.*, the more water of crystallization the more intense the fluorescence, as in the case of the lithium manganese acetates. The nonfluorescing compounds of lower valence or those without the "uranyl" oxygen, as well as the sodium carbonate and zinconium oxide solutions of uranic oxide, which, though having peculiar and characteristic absorption, do not fluoresce, were not taken up. The particular groups taken up largely were the nitrates, chlorides, sulphates, and acetates, with potassium, rubidium, cæsium, ammonium, and sodium in double salts. The phosphates, fluorides, oxalates, and tartrates and some double salts with the bivalent elements were studied in some cases.

The material for use in this investigation was obtained at first from Kahlbaum. Later a number (25) of compounds were prepared by G. O. Cragwall in the Chemical Laboratory of Cornell University. The remainder were prepared by the authors. Cragwall's material was a large quantity of uranium residue originally from Kahlbaum, during the purification of which by conversion to ammonium diuranate and hen to the chloride the first ammonium uranyl chloride crystals with the resolved spectrum were observed.

The material used by the author was chiefly uranyl nitrate hexahydrate purchased as chemically pure, but which was found to contain noticeable quantities of sodium nitrate crystals. This was dissolved in water, precipitated with ammonium hydroxide, washed by decantation to incipient suspension, to which HCl was added until nearly all the precipitate was dissolved. This leaves most of the iron in suspension if present in small quantities and was used to separate out iron in reworking material contaminated from spatulas, etc. On boiling this solution, if much iron is present it further coagulates and can be filtered, but if the acid concentration is low enough, quite a portion of the uranium separates as H_2UO_4. The chloride solution was precipitated again with ammonia, washed, and redissolved in nitric acid. The nitrate was evaporated until the salt (trihydrate) began to crystallize out, and was then carefully heated until decomposition took place, with the formation of the red uranic oxide. Care was taken not to form the black uranous uranic oxide U_3O_8 by overheating. The red oxide containing some undecomposed nitrate was digested with water, which converted the oxide into the hydroxide, or acid H_2UO_4, a bright yellow powder. This was washed free from nitrate by decantation and air-dried and formed the major part of the material used.

Some stock uranyl acetate was used, but as this usually contains sodium acetate also, it is not advisable when preparing sodium-free salts to be compared with sodium triple salts.

Some material was also precipitated as the oxalate, but this does not give complete precipitation, and as it gives the black U_3O_8 on ignition, which is not as readily soluble, it is not of much value except for preparing oxalates.

For making triple sodium acetates, some material was precipitated as the sodium uranate, dissolved in sodium carbonate, and the solution treated with acetic acid, from which the sodium uranyl acetate crystallizes, leaving the sodium acetate in solution with very little waste uranyl salt.

NITRATES.

URANYL NITRATE.

This is the commonest and best known of the uranyl salts, crystallizing ordinarily as the hexahydrate, which readily forms large, clear crystals by cooling or evaporation. It is prepared by dissolving either the uranic oxide or hydroxide H_2UO_4 or the uranous uranic oxide U_3O_8 in nitric acid and crystallizing. This salt shows strikingly the property of most of the uranyl salts of strong acid, of dissolving noticeable amounts of the oxide in the neutral solution, so that a clear solution may be strongly basic. This oxide precipitates on heating or evaporation.

Uranyl Nitrate Hexahydrate.

$UO_2(NO_3)_26H_2O$.

The complete description[1] of the crystal properties of this hydrate are given in Groth's Chemische Krystallographie, II, page 142.

System rhombic; axial ratio $a : b : c = 0.8737 : 1 : 0.6088$. Forms b (010), a (100), making short rectangular prisms with pyramidal ends formed by b (111), usually cut also by q (011), making a a six-sided face and b eight-sided. The prism (110) was observed on one crystal which was deformed by growing near another. Specific gravity, according to Boedeker (1860), is 2.807.

No statement is made as to cleavage, but it was found that very slight temperature changes produce a spontaneous cleavage, generally along q (011), so that the crystals can not be handled on a cold day and immersion in liquid air completely powders them.

The optical properties are double refraction +, plane of axes b (010), acute bisectrix the c axis, apparent angle of optic axes 67° to 69°, mean index β 1.495 to 1.502. The pleochroism, according to Schabus, gives bright yellow-green parallel to a, b greenish yellow, c deep citron yellow.

The fluorescence and absorption were investigated by Stokes[2], E. Becquerel, Hagenback,[3] and H. Becquerel.[4] The tribo-luminescence was noticed by Herschel.[5] Wasiljew[6] gives the melting-point of the hexahydrate as 60.2° C. and gives the solubility curve for the hexahydrate in water. Silliman[7] gave

[1] de la Provostage, Ann. der Chim. Phys. (3), 5, 48. 1842.
Schabus, Preischr. Wien (1855), 40.
Sitz. berichte d. A. d. W. Wien, 27, 41. 1857.
Rammelsberg, Neust. Fortsch. in de Kryst. Chem. Leipzig, 58. 1857.
Lang, Sitz. ber. Wien, 31, 120. 1858.
des Cloiseau, Annales des Mines (5), 14, 348. 1858.
Quercigh, Riv. Min. crist. Ital., 4, 6–14. 1915.

[2] Stokes, Phil. Trans., 142, 517, 520. 1852.

[3] Hagenback, Poggendorff's Annalen, 146, 395. 1872.

[4] H. Becquerel, Ann. Chim. Phys. (6), 14, 230. 1888.

[5] Herschel, Nature, 60, 29. 1899.

[6] Wasiljew, Chem. Zentralblatt 14, 2, II, 1527. 1910. Jour. Russ. Phys. Chem. Ges. 42, 577. 1910.

[7] Silliman, Amer. Jour. Science (2), 27, 14. 1859.

59.5° C. which is probably not as accurate. Lowenstein[1] gives the vapor-pressure of the saturated solution as 18 mm. approximately at 25° and the pressure of the equilibrium between hexahydrate and trihydrate as over 4 mm. The author found the two hydrates to be stable together at 5 mm. at 20°. The result is that the crystals always effloresce and fall to a yellow powder if left in the air, in the winter especially if the sun falls on them, and may deliquesce in the summer. Lescouer[2] gives the vapor-pressure of the solution at 6° as 12 mm. and for the trihydrate below 3 mm. The author found that the hexahydrate dissolved in various concentrations of nitric acid at 20° C. in the following ratio: 1.6 grams of hexahydrate in 1 gram of 10 per cent HNO_3, 1.15 grams in 20 per cent, 0.8 gram in 30 per cent, 0.65 gram in 40 per cent to 70 per cent HNO_3. The values have not been determined accurately above 40 per cent on account of the complications due to the occasional formation of the trihydrate.

These crystals were usually grown by evaporation in the room. For work on the polarization they were grown in thin plates tabular on *a* or *b* by putting small seed crystal in a solution of the depth desired for the thickness of the crystal, in the position desired.

Uranyl Nitrate Trihydrate.

$UO_2(NO_3)_2 3H_2O$.

This hydrate is mentioned by Lescouer[3] and by Ditte[4] as being formed when the hexahydrate is heated to boiling. Drenkman[5] and Schultz-Sellack[6] found that on adding the hexahydrate to strong nitric acid and crystallizing by cooling or evaporation the trihydrate was obtained. Lebeau[7] also obtained it by heating the hexahydrate on the water-bath or by evaporating the nitric acid solution in a dessicator over H_2SO_4 or KOH. Marketos[8] mentions it as formed directly from the hexahydrate over sulphuric acid in a dessicator, as does also Forcrand.[9] As can be deduced from the vapor-pressure data of Lowenstein and the author, this air-drying takes place as soon as the vapor-pressure of the water in the atmosphere goes below 5 mm. The best crystals are obtained by slow evaporation of the solution of the hexahydrate, dried on the water-bath in concentrated nitric acid in a dissicator over sulphuric acid and caustic potash or quicklime.

The crystalline form was measured by G. Wyrouboff,[10] who obtained his crystals by evaporating the neutral solution at 65°.

System triclinic; axial ratio, $a : b : c = 1.7753 : 1 : 1.$ 4104.

α 85°35′; β 94°12′; γ 81°44′.

Forms *p* (001), making plates with *h*′ (100), *a*′ ($\bar{1}01$), and $a^{\frac{1}{2}}$ (201) on the edges, and $c^{\frac{1}{2}}$ ($\bar{1}11$) and $b^{\frac{1}{2}}$ ($\bar{1}\bar{1}1$) oblique-angled ends.

The specific gravity was found to be 3.345. No cleavage has been noticed, although the crystals are likely to form with irregular cracks across or radiat-

[1] Lowenstein, Zeit. Anorg. Chem. 63, 105–107. 1909.
[2] Lescouer, Ann. Chim. Phys. (7), 7, 429. 1896.
[3] Lescouer, *loc. cit.*
[4] Ditte, Ann. Chim. Phys. (5), 18, 337. 1879. Compt. Rend. 89, 643. 1879.
[5] Drenkman, Jahrsber der Fortschritt Chem., 256. 1861.
[6] Schultz-Sellack, Jahrsber. Fort. Chem., 365. 1870; Zeit. fur Chem., 646. 1870.
[7] Lebeau, Bull. Soc. Chim. (4), 9, 299. 1911.
[8] Marketos, Comptes Rendus, 155, 210. 1912.
[9] Forcrand, Comptes Rendus, 156, 1044, 1207, 1954. 1913.
[10] Wyrouboff, Bull. Soc. fran. Mineral, 32, 340. 1909.

ing from the seed. Schultz-Sellack gives the melting-point as 120° and Wasiljew as 121.5° C. It is really only a partial melting-point, as the dihydrate is not completely soluble in the resulting solution. The solubility of the trihydrate in water above 60° or in nitric acid has not been determined, although Ditte gives a solubility of 14.39 parts of the trihydrate in monohydrated (91 per cent) nitric acid.

Uranyl Nitrate Dihydrate.

$UO_2(NO_3)_2 2H_2O$.

Ordway describes the dihydrate as resulting by boiling off the fused hexahydrate, which Lowenstein confirms. The latter finds it as the product of 6 days' dihydration over sulphuric acid of over 80 per cent strength, although Fourand finds 6 days required in a vacuum over strong sulphuric. Lebeau finds powdered hexahydrate converted to dihydrate in a vacuum desiccator with concentrated sulphuric acid in 72 hours. Lebeau finds that on treating the hexahydrate with ether, two layers are formed, of which the ethereal layer can be dried with anhydrous calcium nitrate, which leaves the dihydrate on evaporation. It is to be noted in this connection that the ethereal solution, which is also used for separating uranium X, can not be boiled off, as it decomposes with explosive violence after some heating, liberating copious nitrous fumes.[1] Lebeau also obtains crystals with ether of crystallization at 10° and −70°. The dihydrate may also be formed by adding dry UO_3 to fuming nitric acid (92 per cent), from which solution it is readily recrystallized. Wasiljew, crystallizing the dihydrate from fuming nitric acid (s. g. 1.502), finds quadratic tables of the rhombic system with strong fluorescence. The author found yellow plates with marked fluorescence at lower temperatures of probably rhombical pinacoid and pyramid, with some other forms. The crystals weather so rapidly, having a vapor-pressure of 0.2 mm., according to Lowenstein, that changing from one closed vessel to another usually tarnishes them so that little can be done in the way of measuring, handling for cleavage, etc. Wasiljew gives the melting-point as 179.3°. The mixture of dihydrate and solution obtained by melting the trihydrate goes over to solution at about 160° and then goes unchanged except for slight boiling to 240°.

Uranyl Nitrate Anhydrous.

$UO_2(NO_3)_2$ or $UO_3.N_2O_5$.

Marketos produced anhydrous uranyl nitrate by heating the nitrate to 170° to 180° C., since total decomposition took place at 200°, and passing over it dry carbon dioxide saturated with nitric-acid vapors by bubbling through concentrated nitric and sulphuric acids. This produced a yellow amorphous salt soluble in water which decomposed ether, with the liberation of nitrous vapors. Forerand found that long heating above 125° C. in a current of dry carbon dioxide produced basic anhydrous nitrate and below 100° only a monohydrate. Twelve hours at 165 in a current of carbon dioxide charged with nitric-acid vapors gave $UO_2(NO_3)_2 + 1/31H_2UO_4$.

The method evolved for producing anhydrous uranyl nitrate was to place in a train of U-tubes a tube containing uranic oxide made by heating the hydroxide or acid H_2UO_4 until it began to turn red and distilling over it nitric

[1] Muller, Chem. Ztg., 41, 439, 1917; 40, 30, 1916.

anhydride, N_2O_5. This was accomplished by having a reaction flask fitted to the system by a ground-glass joint, in which were placed phosphorus pentoxide and fuming (92 per cent) nitric acid in calculated amounts. From this, on heating to 50°, the N_2O_5 distilled out and was condensed by freezing mixture in the first U-tube, which served as a reservoir. When this was filled with solid N_2O_5 and a two-liquid layer of N_2O_5 and HNO_3, the flask was removed, the joint covered by a cap, and the anhydride distilled over on the uranic oxide by placing the reservoir tube in a bath of hot oil. No reaction took place between the oxide and the acid until the oxide tube was in turn put in the oil-bath and the anhydride boiled off into the last tube, which served as a second reservoir for the acid. As soon as the acid began to boil the reaction took place, producing a vivid green fluorescence and a light yellow color instead of the reddish oxide. The anhydride could be distilled off and run back over while holding the tube with the uranyl nitrate at any temperature. Also, any acid which did not solidify could be poured off and the remaining N_2O_5 run back over the nitrate, insuring absolute freedom from water. The resulting compound was found to be stable up to 180°, at which temperature it broke up into N_2O_5 and UO_3, which could be recombined if the temperature was lowered. Distilling the acid on and off was performed several times with one specimen, examining the spectra each time, which showed first the anhydrous salt fluorescence and then none for the oxide.

DOUBLE NITRATES.

Meyer and Wendel[1] prepared double salts of ammonium, potassium, rubidium, cæsium nitrates with uranyl nitrate. These crystals were described by Steinmetz.[2] They were grown from a solution in nitric acid and were of the type $KUO_2(NO_3)_3$. Rimbach[3] endeavored to determine the solubility of these salts in water at various temperatures. He found large crystals in the ammonium and potassium solutions unlike those of Meyer and Wendel which were measured by Sachs[4] and assigned formulæ like those of Meyer and Wendel, but since they were alike were called isomorphous and the α forms of NH_4 and $KUO_2(NO_3)_3$. Examination of the spectra of these forms in the laboratory indicated and Sachs's data itself proves that the α form is simply uranyl nitrate hexahydrate.

In attempting to grow crystals according to Rimbach's method which would not be uranyl nitrate, however, two new forms were discovered containing two molecules of alkali nitrate to one of uranyl nitrate. In the process of growing the potassium salt for experimental purposes, still a third was found, but so rarely that it was not studied.

In order to find out the conditions under which the various salts were formed, a series of solubility determinations were undertaken, being run at constant temperature of 20° C. in a thermostat, with varying percentages of aqueous nitric acid as a solvent.

From these incomplete results it will be seen that from solutions of less than 30 per cent nitric acid and less than 1 molecule of uranyl nitrate to 1 of potassium nitrate, potassium nitrate only will crystallize; that in a 1 to 1

[1] Meyer and Wendel, Ber. d. d. Ch. Ges., 36, 4055. 1903.
[2] Groth's Chem. Kryst, II, 150.
[3] Rimbach, Ber. d. d. Ch. Ges., 37, 472. 1904.
[4] Sachs, Zeit. f. Krys., 38, 497. 1904.

solution above 40 per cent the so-called γ form or monopotassium salt will appear. In the 1 of uranyl nitrate to 2 of potassium nitrate, the double nitrate crystallizes only above 50 per cent of nitric acid, and as the δ phase or the dipotassium salt and the metastable phase at this concentration is the γ form. Presumably at higher concentrations of potassium nitrate the last-found and undetermined form would appear.

Grams of solute in 100 grams of solvent.

Solvent (p. ct. HNO_3).	$KNO_3.UO_2(NO_3)_2$.				$2KNO_3.UO_2(NO_3)_2$.				KNO_3.
		Solid phase.		*Solid phase.*		*Solid phase.*		*Solid phase.*	
0	85.5	KNO_3	.....	.....	62.9	KNO_3	.....	.....	31.4
10	82.0	KNO_3	.....	.....	52.2	KNO_3	.....	.....	19.1
20	99.8	KNO_3	.....	.....	45.7	KNO_3	.....	.....	14.5
30	89.0	Hex	89.5	γ	51.8	KNO_3	.....	.....	11.4
40	81.3	γ	.....	.....	67.2	KNO_3	.....	.....	15.2
50	54.0	γ	.....	.....	52.3	δ	57.5	γ	18.6
60	33.9	γ	.....	.....	.....	.....	.....	.....	19.6
70	.....	.....	.....	.....	.....	.....	.....	.....	29.6
80	.....	.....	.....	.....	.....	.....	.....	.....	34.2
90	.....	.....	.....	.....	.....	.....	.....	.....	48.8

Solvent (p. ct. HNO_3).	$NH_4NO_3.UO_2(NO_3)_2$.				$2NH_4NO_3.UO_2(NO_3)_2$.				$NH_4.NO_3$
		Solid phase.		*Solid phase.*		*Solid phase.*		*Solid phase.*	
0	165	Hex.	.....	.....	251	Hex.	380	β	191
10	128.6	Hex.	.....	.....	201	Hex.	380	β	151
20	80.3	Hex.	144.5	β	150	Hex.	215	β	127
30	68.2	Hex.	144	β	144	Hex.	150	β	104.8
40	60.5	Hex.	95.6	β	98.2	β	.....	.....	86.4
50	61.4	β	.....	.....	58.0	β	.....	.....	76.5
60	38.6	β	.....	.....	35.6	β	.....	.....	.....

Solid phases appearing are:
Potassium nitrate, KNO_3.
Ammonium nitrate, NH_4NO_3.
Uranyl nitrate hexahydrate, $UO_2(NO_3)_2\ 6H_2O$, Hex.
Monopotassium uranyl nitrate, $KUO_2(NO_3)_3$, γ.
Dipotassium uranyl nitrate, $K_2UO_2(NO_3)_4$, δ.
Monoammonium uranyl nitrate, $NH_4UO_2(NO_3)_3$, β.

From solutions 1 molecule of uranyl nitrate to 1 of ammonium nitrate, uranyl nitrate hexahydrate crystallizes unless the per cent of nitric acid is at least 50, above which the β or monoammonium form crystallizes, which is metastable practically to water solution. From 2 molecules of ammonium nitrate to 1 of uranyl the hexahydrate crystallizes up to 40 per cent, above which the β form appears, which is also metastable to pure aqueous solution. It will be noted that while potasisum nitrate is about as soluble as uranyl nitrate and the phase in equilibrium with the more acid solutions corresponds to the composition of the solution, the ammonium nitrate is much more soluble and not only does not form the solid phase in case uranium is present, but does not form the diammonium salt from solutions of that composition. Laboratory experience showed that a large excess of ammonium nitrate and

rather low acid concentration was necessary to produce this form. These higher ratios of ammonium nitrate should be investigated.

These results do not check well with those of Rimbach, who presumably crystallized considerable portions of the salt, instead of determining the phase with which the solution was in equilibrium by the addition of seeds of known phases. They do not, however, materially conflict with those of Engel[1] in the case of the solubility of potassium nitrate in nitric acid, where the solubility is found greater at 20° than at 0° in dilute solutions and less in highly acid solution.

The mono or acid forms of the double potassium ammonium salts and the corresponding rubidium and cæsium salts were found to be as described by Sacks from the preparation of Meyer and Wendel. There is no indication that the corresponding double salts containing 2 atoms of rubidium or cæsium could not be produced by using solutions similar to that used for the dipotassium salt.

Other double uranyl nitrates with other bases than the four alkalies discussed do not seem to form, with the exception of thallium, which is reported by Meyer and Wendel as forming but being non-fluorescent, as the double thallous sulphate is. Sodium nitrate crystallizes side by side with the hexahydrate or trihydrate, according to the acidity of the solution, but no conditions were found under which the two salts would crystallize together. Silver, cadmium, zinc, calcium, barium, and magnesium were also tried without success, although a modification of the hexahydrate spectrum was produced by the calcium and magnesium. Meyer and Wendel also tried lithium, sodium, and the bivalent metals without formation of double salts.

Monopotassium Uranyl Nitrate.

(γ form) $KUO_2(NO_3)_3$.

These crystals were prepared by Meyer and Wendel by crystallizing potassium nitrate and uranyl nitrate in equal proportions from a nitric-acid solution. The crystals were examined by Steinmetz.

System rhombic; axial ratio 0.8541 : 1 : 0.6792.

Thick tabular combinations of *c* (001), *m* (110), with subordinate forms of *b* (010), *s* (102), *o* (111), sometimes *a* (100), and rarely *a* (011) and 122. Steinmetz and Sykes report good cleavage on *b*, and good cleavage was also observed on *a*. The specific gravity was found to be 3.503. Crystals of this form are stable at 20° if the partial pressure of the water-vapor is not over 9 mm. Hg, but at that point begin to deliquesce, changing to a whitish yellow chalky mass. On heating the crystals, yellow crusts begin to form on the crystals at 150°, violent decrepitation begins at 200°, and decomposition with liberation of nitrous fumes at 270° C.

According to Steinmetz, the plane of the optical axes is *c* (001), acute bisectric *a*. Axes visible through (110).

The best crystals were obtained by cooling of hot solutions supersaturated 2 grams in 50 c.c. in glass-stoppered bottles.

The composition as determined by Meyer and Wendel was $KUO_2(NO_3)_3$. An ignition run to check this gave 65.13 and 64.82 per cent, the theoretical form $K_2U_2O_7$ being 67.29, the low values being due to loss by decrepitation.

[1] Engel, Comptes Rendus, 104, 913. 1887.

Dipotassium Uranyl Nitrate.

(δ form) $K_2UO_2(NO_3)_4$.

These crystals appeared, after a year of effort to obtain crystals from neutral solution which were not hexahydrate, in a slightly acid solution containing an excess of potassium nitrate. It shows marked reluctance to appear and does not grow well if the room temperature is below 20° C., the hexahydrate forming instead, but above that temperature gives fine crystals, especially if seeded, although it does not grow as rapidly as the other members of the group.

System monoclinic; axial ratio $a : b : c = 0.6394 : 1 : 0.6190$; $\beta = 90 \pm$.

	calc.	obs.
$c : a = 001 : 100 =$	90° 0′	
$p : p' = 331 : 3\bar{3}1 =$	63° 30′	
$c : p = 001 : 331 =$	77° 38′	
$c : d = 001 : 101 =$	50° 1′	52° 52′
$c : o = 001 : 133 =$	42° 43′	43° 10′
$c : q = 001 : \bar{1}31 =$	59° 22′	60° 39′
$o : o = 133 : 1\bar{3}3 =$	73° 58′	73° 15′
$o : p = 133 : 331 =$	42° 58′	42° 48′
$o : p' = 133 : 3\bar{3}1 =$	84° 19′	84° 0′
$o : \pi = 133 : 232 =$	19° 19′	20° 44′
$o : q = 133 : \bar{1}31 =$	52° 3′	51° 50′
$o : d = 133 : 101 =$	45° 38′	47° 35′
$p : \pi = 331 : 232 =$	23° 39′	22° 49′
$p : d = 331 : 101 =$	38° 42′	38° 25′
$p : q = 331 : 13\bar{1} =$	43° 37′	42° 12′
$d : q = 101 : 131 =$	56° 31′	56° 17′
$d : \pi = 101 : 232 =$	37° 6′	38° 56′
$d : m = 101 : 230 =$	61° 7′	62° 48′

These axes are probably not those of the space lattice, being taken from the first habitus observed, which formed in a solution having barely enough potassium nitrate to produce this phase, and consisted of *e* (001), *o* (133), and *p* (331) meeting in a point in front which was sometimes cut off by *a* (100), usually accompanied by *d* (101). π sometimes occurred between *o* (133) and *p* (331) and *q* (131) between *o* 133 and *p* 311; *b* (010) and *m* (230) were found in measurement. One crystal showed *c*, *o*, *p*, *d*, and *d′* (101), *a* and probably *q* and (11$\bar{1}$). Most of the crystals grown later had a prismatic or needle habitus in which *p* (331) was the predominant form, with small *e* faces on the ends and occasionally some of the other forms. All faces on these crystals gave reflections which appeared in the goniometer as a flattened figure 8, and best agreements were found in the angles taken from the outside of every pair of readings. In case the whole figure did not appear, results were unsatisfactory.

On dissolving a large crystal in the mother-liquor by heat, *c* (001) was untouched, *d* (101) was left even and a little pitted, and the edge between *p* (331) and *o* (133) was rapidly dissolved, leaving the deepest etching where these met at *d* (101).

No conspicuous cleavage was noticed.

The specific gravity was found to be 3.359.

On heating crystals of this phase, they first decrepitate to an opaque yellow powder at 200° C., which, at 260° C., flows together. Above this temperature decomposition sets in, with the evolution of nitric fumes. Various colored masses result, deep red U_3O_8, bright red UO_3, bright yellow K_2UO_4, and on cooling a beautiful rose pink pervades the mass.

This phase does not change over concentrated sulphuric acid, *i. e.*, has zero vapor-pressure at 20° C., but over acid corresponding to 11 mm. of mercury of partial pressure of water-vapor it turns whitish without becoming moist, probably due to the formation of KNO_3 and $UO_2(NO_3)_2\ 6H_2O$. This is the same pressure at which the diammonium salt deliquesces.

The refractive index of dipotassium uranyl nitrate given by the faces (001) and *d* (101) were found to be 1.5422 for light vibrating parallel to the *b* axis

and 1.5349 for light vibrating in the *ac* plane 26° 34½′ from *a* toward *c* in the "acute" angle β.

The composition was investigated by igniting to K_2UO_4 and by washing out the K_2SO_4 from sulphuric-acid solution precipitated with NH_4OH and weighing the resulting U_3O_8 and K_2SO_4.

	Theoretical.	First.	Second.
	p. ct.	*p. ct.*	*p. ct.*
K_2UO_4..	63.78	64.61	63.52
K_2SO_4...	47.09	46.85	47.03
U_3O_8....	29.19	30.36	29.01

The best crystals were obtained by cooling solutions supersaturated 1 gram in 100 c.c.

MONOAMMONIUM URANYL NITRATE.

β form $NH_4UO_2(NO_3)_3$.

This salt forms from solutions containing uranyl nitrate and ammonium nitrate at room temperature if the acid-content is high and from water at higher temperatures.

System trigonal; axial ratio $a : c = 1 : 1.0027$ (α 97°6′). The forms are prismatic combinations of prism *a* (1120) with the rhombohedron *r* (1101) on the end, on the edges of which occur *s* (1012).

	Theory.	Steinmetz.	W.
$r:r = 1101 : \bar{1}011$ ...	81° 47′	81° 54′	82° 8′
$s:s = 01\bar{1}2 : \bar{1}102$ ...	51° 19′	51° 30′	51° 36′

The column headed Theory gives the values for a substance having an axial ratio $a : c = 1 : 1$, the close approximation to which makes this a remarkable case and probably indicates something concerning the structure.

Twins were observed in which the contact plane was *s* $\bar{1}102$ and the twinning axis, the axis of reference to which *s* was parallel, making the angle between the two unique axes 119°54′ and giving the crystal the appearance of a flat hemimorphic orthorhombic crystal. The angle between the two *r* ($1\bar{1}01$) faces was calculated to be 21°32′ and found to be 21°±.

Crystals of this form are stable in dry air, but begin to deliquesce and change to a light yellow chalky mass if the vapor-pressure of water is above 9 mm. Hg.

Intense pleochroism was observed in crystals about 0.01 mm. thick on a microscope slide, when they occurred lying on a prism face, the light vibrating parallel to the unique axis appearing white, *i. e.*, less yellow than the mother-liquor in which the crystal lay, while that ordinary ray appeared a deep yellow.

The monopotassium and monoammonium crystals separate from the same solution, there being no tendency to form mixed crystals.

The composition of the crystals was checked as being the same as that given by Meyer and Wendel by igniting to the oxide. Theory, 59.22 per cent found, 58.97, and 58.86.

Diammonium Uranyl Nitrate.

α form $(NH_4)_2UO_2(NO_3)_4 2H_2O$.

This phase crystallizes from slightly acid solutions of uranyl nitrate containing a large excess of ammonium nitrate. Its solubility increases very rapidly with rising temperature, until at about 60° C. the uranyl nitrate dissolves out, leaving a residue of ammonium nitrate. This salt crystallizes very readily in large sulphur-yellow perfect crystals of 5 or 10 grams from a volume of solution that only gives 1 or 2 grams of monoammonium salt and crystallizes best if the room temperature is 10° to 15°. The fluorescence is very faint at 20° C., but increases rapidly below 0°, becoming stronger than that of the monoammonium salt at liquid-air temperatures.

System monoclinic axial; ratio $a : b : c = 0.8419 : 1 : 0.5594$; β 94°55′. The habitus resembles that of a cube with octahedron, the forms being *c* (001), *a* (100), *b* (010), and *o* (111). The faces ρ (110) were also occasionally observed, and possibly (211).

No cleavage was observed, thus increasing the resemblance to sulphur crystals. However, on heating rapidly, the crystals fill with cracks, and consequently seeded crystals often have a large single crack more or less parallel to *a* (100).

Etch figures produced by resolution in a crystal in the mother-liquor were found once, the distinct forms being on *b* (010), with two rounded faces meeting in a line in the bottom as though a lens had been pressed in. The bottom edges were all parallel and about halfway between the edges of *b* (010) and *o* (111), *i. e.*, parallel to (102).

The specific gravity was found to be 2.777.

When these crystals are heated slowly they break down at about 140°, giving a pasty mass full of bubbles, which clears up slightly at 220°, but does not give a clear solution below 240°. On cooling, bright green crystals of the monoammonium salt form in a background of white ammonium nitrate.

Crystals of this phase placed over sulphuric acid with a pressure of water-vapor of 4 mm. started to lose water, turning to a whitish powder, and continued to do so slowly at 5 mm., although then they do not start. Placed over sulphuric acid with a vapor-tension of 11 mm., they deliquesce rapidly, soon going completely into solution.

The refractive index was observed in two different directions, using natural faces. First, between 111 and $\bar{1}1\bar{1}$ giving the light vibrating in the *ac* plane nearly parallel to the edge *o* 111 : *o* $1\bar{1}1$, with an index of 1.546, and that at right angles to the *ac* plane as 1.639; between the faces *b* 010 and *o* 111, giving for light appearing on *b* to vibrate nearly parallel to edge between *b* (010) and *o′* $1\bar{1}\bar{1}$ as 1.508, and at right angles to that 1.619.

The composition was determined by ignition to U_3O_8, which gave 47.68 and 47.62 per cent against theoretical 47.58.

URANYL CHLORIDE.

Neither the monohydrate $UO_2Cl_2H_2O$ described by de Coninck[1] as being formed by evaporating the solution prepared by precipitating the sulphate solution nor the trihydrate, which, according to Mylius and Dietz,[2] forms from

[1] de Coninck, Comptes Rendus, 148, 1769. 1909.
[2] Mylius and Dietz, Ber. d. d. Ch. Ges., 34, 2774. 1901.

the evaporation of the solution of the oxide in hydrochloric acid, were successfully prepared and freed from the sirupy mother-liquor so as to give good fluorescence spectra.

Double Chlorides.

The alkali double chlorides, as was discovered early in this investigation in the case of the ammonium salt, give resolved spectra at room temperature. This makes the group quite important. The four double salts of ammonium, potassium, rubidium, and cæsium were prepared. Attempts were made to prepare the double salts with silver, cadmium, zinc, and calcium, and also hydrazine and hydroxylamine, but resulted in each case in the formation of the crystals of the chloride added, in a sirup or mat of the uranyl chloride. The silver was sealed in a tube with a strong HCl solution as solvent, but although remaining white did not dissolve and recrystallize. The tetramethyl and tetraethyl ammonium chlorides described by Rimbach were not made.

The alkali double chlorides in general were grown by evaporation in a desiccator in presence of an excess of HCl, which is necessary to prevent hydrolysis of the uranyl chloride. This forces back the solubility of the alkali salt, so that the solutions usually contain an excess of uranyl chloride. The crystals, if allowed to stand in the open air, readily give off acid, turning the color of any indicator paper on which they are placed and in moist atmosphere deliquesce readily, the sirupy uranyl chloride running away from a skeleton of alkali chloride.

Potassium Uranyl Chloride.

$K_2 \cdot UO_2 \cdot Cl_4 \cdot 2H_2O$.

This salt was described by de la Provostage[1] as occurring in hexagonal tables on c (001) bounded by o (111), w ($1\bar{1}\bar{1}$), m (110), μ ($1\bar{1}0$), b (010), q (021). The crystals measured by Rammelsberg were mostly prismatic along the a axis. The first type were those used in this work, although crystals tabular on b (010) were fairly frequent.

System triclinic; axial ratio, $a:b:c:=0.607:1:560$. $\alpha=80°41'$; $\beta=77°42'$; $\gamma=91°18'$.

	$K_2UO_2Cl_4.2H_2O$.			$(NH_4)_2UO_2Cl_4.2H_2O$.	
	Calculated.	de la Provostage.	Rammelsberg.	Grailich.	W.
$m : b = (110) : (010)$ ...	60° 28′	60° 30′	60° 52′	60° 30′ ±	61° 0′
$\mu : b = (1\bar{1}0) : (0\bar{1}0)$ ...	61° 33′	61° 10′	.....	.....	60° 48′
$\mu : c = (110) : (001)$ ...	83° 48′	83° 55′	.....	83° 0′	85° 26′
$b : c = (010) : (001)$ ...	99° 15′	.....	98° 53′	.....	99° 34′
$q : c = (012) : (001)$ ...	55° 21′	55° 30′	55° 45′	.....	56° 22′
$o : c = (111) : (001)$ ...	.....	60° 15′	.....	.....	59° 40′
$w' : c = (\bar{1}11) : (001)$ ...	.....	46° 55′	.....	.....	47° 4′
$o : b = (\bar{1}11) : (010)$ ...	.....	81° 0′	.....	80° 0′	.....
$w' : b = (\bar{1}11) : (010)$ ...	.....	75° 20′	.....	75° 30′	.....
$w' : q = (111) : (012)$ ...	46° 17′	46° 5′	.....	.....	.....
$o : \mu' = (111) : (\bar{1}10)$ ...	66° 33′	66° 45′	.....	.....	.....
$m : c = (110) : (001)$ ...	.....	.....	.....	.....	76° 8′

The properties of the crystals were similar to those of the ammonium salt, although the crystals seemed to grow larger more readily.

[1] de la Provostage, Ann. Chim. Phys. (3), 6, 165. 1842.

In the work of Jones and Strong,[1] it was found that the absorption bands persist far out into the red, only the intensity decreases with such rapidity that great depths of solution were required to show them. To try this out in the case of the resolved spectra of the chlorides, thick layers were built up of several crystals and found out to hold. A very deep crystal was grown in a glass tube ground into the bottom of an inverted bottle-neck which held the solution. This crystal, which was 3 cm. thick, was never tried.

Another investigation which was never finished was that of the character of the spectra of mixed crystals, of which potassium ammonium salt $K{\cdot}NH_4{\cdot}UO_2{\cdot}Cl_4{\cdot}2H_2O$ was prepared as an example.

Ammonium Uranyl Chloride.

$(NH_4)_2{\cdot}UO_2{\cdot}Cl_4{\cdot}2H_2O$.

The crystal forms of this salt are practically identical with that of the potassium salt, as shown by the table of angles under that salt. Intense pleochroism is noticed in this crystal when viewed through the *c* (001) face if the crystal is about 1 mm. thick. The light vibrating parallel to the *b* (010) edge of the face, *i. e.*, parallel to the axis, is so little absorbed as to appear white and is also least refracted. The light vibrating nearly parallel to the *b* axis is strongly absorbed in the blue-violet and appears deep yellow even in these crystals. The refractive indices parallel to *a* and nearly parallel to *b* and *c* were measured on prisms cut so that light traveled parallel to the *c* face and at right angles to it. It happens that the letters of the refractive indices correspond to the axes to which they are nearest.

	a	*b*	*c*
λ720.	1.564–1.566	1.619	1.622
λ580.	1.566–1.574	1.633	1.637
λ500.	1.576–1.581	.....	1.650

The absorption is so great parallel to *b* that the value for λ 500 could not be obtained.

Rubidium Uranyl Chloride.

$Rb_2{\cdot}UO_2{\cdot}Cl_4{\cdot}2H_2O$.

This is similar to the potassium and ammonium salts; although no measurements were taken, the crystals could not be distinguished, except by knowing the individual crystals.

Cæsium Uranyl Chloride.

$Cs_2UO_2Cl_4$.

The salt was crystallized as above from a solution containing cæsium chloride and uranyl chloride and presented a distinctly different appearance from the other members of the group. This is accounted for by the composition, which, according to Rimback, Wells and Boltwood,[2] is the anhydrous chloride instead of containing 2 molecules of water, as with the other salts. The crystals were elongated rhombs of yellow color, showing less fluorescence than the other salts. Under the polarizing microscope they showed a striking

[1] Jones and Strong, Carnegie Inst. Wash. Pub. No. 130, 90.
[2] Wells and Boltwood, Zeit. Anorg. Chem., 10, 181. 1895.

resemblance to gypsum, possessing the "fish-tail" twins and approximately the same angles and appearing different only in the yellow absorption. The crystals were so universally twinned that the interfacial angles could not be determined certainly. The largest face was b (010), with the two prism faces m (110) and μ ($1\bar{1}0$), and, as determined by measurement, practically all the end faces were d (011), r (031), s ($0\bar{3}1$), although these usually appeared twice on a crystal, and other faces indicated by the measurement were q 111, x ($1\bar{1}1$).

System triclinic.

$b:m = 010:110 = 49°\ 7'$
$b:\mu = 010:1\bar{1}0 = 50°\ 50'$
$b:d = 010:011 = 40°\ 31'$
$b:r = 0\bar{1}0:0\bar{3}1 = 67°\ 48'$
$b:s = 0\bar{1}0:0\bar{2}1 = 57°\ 41'$

$m:q = 110:111 = 43°\ 41'$
$m:r = 1\bar{1}0:0\bar{3}1 = 86°\ 49'$
$\mu:r = 1\bar{1}0:031 = 44°\ 0'$
$\mu:x = \bar{1}10:\bar{1}11 = 75°\ 24'$

The refractive index was determined through the faces b (010) and μ ($1\bar{1}0$), the more deviated ray vibrating at an angle of about 15° from the prism edge toward the a axis.

λ720	1.618	1.692
λ580	1.625	1.695
λ500	1.634	1.714

The index was also determined through the faces b ($0\bar{1}0$) and d (011), the less-deviated ray vibrating parallel to this prism edge.

λ580	1.614	1.691
λ580	1.622	1.698

Uranyl Sulphate.

$UO_2SO_4 \cdot 3H_2O$.

This salt was prepared by Cragwall, presumably as the trihydrate. On recrystallization of Kahlbaum material two forms appeared, a yellow opaque needle-mass tending to replace the bright green fluorescent grains. The yellow needles became more numerous on adding sulphuric acid, so uranic oxide was added to saturation, which proved to be in excess on evaporation. The bright green fluorescent crystals were difficult to keep, as they dried out readily in the air. Microscopic examination of the Cragwall preparation showed needles with parallel extinction and greater absorption and greater index the long way of the crystals, while the angle of the optical axes was very large and the sign positive.

The acid sulphate, $H_2UO_2(SO_4)_2 5 4_2O$, was reported by Wyrouboff.[1]

DOUBLE URANYL SULPHATES.

The double sulphates differ from the previous double salts in the occurrence of the sodium salt. The potassium, ammonium, rubidium, cæsium, and thallous salts were also prepared by Cragwall in the form of powders resulting from rapid precipitation by cooling. The potassium and rubidium salts especially showed very strong fluorescence, the sodium and ammonium good fluorescence, the cæsium less, and the thallium practically none, and that was not resolved. Rimbach[2] describes a dipotassium salt which was not prepared and one of hydroxylamine also.

[1] Wyrouboff, Bull. Soc. fran. min. No. 32,351, 1909.
[2] Rimbach, *l. c.*, 479.

These salts were all prepared by crystallization from water of the calculated quantities of the two single salts. Rimbach[1] describes the potassium ammonium and rubidium salts as having each 2 molecules of water of crystallization. On the other hand, de Coninck[2] describes the sodium potassium and cæsium salts as having 3 molecules of water, while the ammonium commonly has 2, but can be made by special conditions with 3 molecules.

Potassium Uranyl Sulphate.

$K_2UO_2(SO_4)_2 2H_2O$.

This salt separates readily on cooling a hot saturated solution of the two salts in equimolecular proportion. This, according to Rimbach, gives the dihydrate, according to de Coninck[3] the trihydrate. The salt prepared in this way is a fine crystalline powder, larger masses being clusters of crystals. A good crystal was discovered in an old solution of known strength. They were then obtained by supersaturating 0.1 to 0.5 gram of salt in 50 to 200 c.c. of solution, seeding, and allowing the tightly stoppered solution to stand from 3 to 6 months, especially in the fall, when the room temperature gradually decreases. The crystals tend to form rosettes, clusters of crystals arising from the middle of the basal pinacoid. The smaller crystals are tabular on the base; the larger ones have large prism faces made up really of repeated pyramids. These are capped by the unit pyramid with brachydome and basal pinacoid.

System rhombic; axial ratio $a : b : c = 0.5889 : 1 : 0.6253$.

	calc.	*obs.*		*calc.*	*obs.*
$b : m = 010 : 110$	32° 1′	32° 13′	$c : p = 001 : 111$	48° 2′	48° 6′
$c : n = 001 : 101$	43° 18′	43° 0′	$c : r = 001 : 332$	59° 3′	59° 30′
$c : o = 001 : 201$	.....	62° 3′	$c : s = 001 : 221$	65° 47′	64° 45′
$c : k = 001 : 011$	30° 30′	30° 19′	$c : t = 001 : 331$	73° 18′	71° 52′
$c : l = 001 : 021$	.....	49° 20′	$c : u = 001 : 441$	77° 20′	77° 25′
$c : q = 001 : 112$	29° 4′	30° 0′			

	𝔄 ∥ to *b*.	𝔅 ∥ to *a*.	ℭ ∥ to *c*.
λ720...	1.5610–1.5627	1.5220	1.5096
λ580...	1.5670–1.5705	1.5266	1.5144
λ500...	1.5785–1.5847	1.5350	1.5202

No pleochroism was observed. Plane of axes *a* (100), obtuse bisectrix normal to base. Double refraction +. Cleavage was observed on the base.

Rubidium Uranyl Sulphate.

$Rb_2UO_2(SO_4)_4 2H_2O$.

The rubidium salt was more fluorescent than the potassium salt and mor difficult to crystallize, so that measurements of it were not obtained. It is, however, completely isomorphous with the potassium salt. The composition, according to Rimbach,[4] is as above, with 2 molecules of water.

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[1] Rimbach, *l. c.*, 478.
[2] de Coninck, Bull. Acad. Roy. Belg., 1904, 1171; 1905, 50, 94.
[3] *Ibid.*, 1905, 50.
[4] Rimbach, *l. c.*, 479.

Cæsium Uranyl Sulphate.

$Cs_2UO_2(SO_4)_2 3H_2O$.

This salt is so insoluble that no crystals could be produced. The Cragwall product recrystallized showed on the microscope-slide square plates about 10 μ in length, which showed a negative uniaxial figure. This salt, according to de Coninck,[1] has the same composition which he finds for the potassium salt, that is, $3H_2O$.

Ammonium Uranyl Sulphate.

$(NH_4)_2UO_2(SO_4)_2 2H_2O$.

This salt was not recrystallized, but showed similar characteristics to the potassium salt. When recrystallized it gave bundles of needles, the vibrations across which were most absorbed and most refracted. Rimbach describes the salt as having 2 molecules of water. The crystals were found to be monoclinic by de la Provostaye.[2]

Sodium Uranyl Sulphate.

$Na_2UO_2(SO_4)_2 3H_2O$.

This salt is described by de Coninck as having 3 molecules of water, which he finds also in the potassium salt. This salt as prepared by Cragwall was not recrystallized, but showed under the microscope one optical axis and the acute bisectrix with positive double refraction. It is, therefore, presumably triclinic, as the acute bisectrix was off normal in both directions.

Thallous Uranyl Sulphate.

$Tl_2UO_2(SO_4)_2 3H_2O$.

This salt was prepared by Cragwall from weighed amounts of the two salts according to Kohn,[3] who found the salt to be of the above composition with probably $3H_2O$. The crystal description by Himmelbauer in the same article gives the system as rhombic, the symmetry from etch figures pyramidal. The forms are the three pinacoids with pyramid faces at the corners which were too small to measure. He observed through (100) in converged polarized light the plane of the axes for red and blue, at right angles the plane of the blue being that of the *a* and *c* axes; for green nearly uniaxial; for red light *a* is the acute bisectrix, the pleochroism on (100) distinct, parallel to *c*, deep yellow; parallel *b* yellowish white, but no noticeable pleochroism on (010). Crystals up to 3 mm. in diameter and 1 mm. thick, produced by slow cooling of the Cragwall salt, showed the axial figure, but it could not be surely seen to agree with the description, due to the intense absorption in the blue and green. The figure might be explained by anomalous dispersion due to the absorption band.

PHOSPHATES.

Uranyl phosphate ($HUO_2PO_4.3\frac{1}{2}H_2O$), which precipitates from uranyl solutions on adding phosphates, possesses no fluorescence. If it is dissolved in an excess of acid it gives a glass or sirup with a brilliant fluorescence which can not be resolved beyond the bands. The sodium double salt was made by adding sodium phosphate to produce $H_2Na_2CO_2(PO_4)_2$ to the uranyl phosphate with an excess of water, which on standing and evaporating gave

[1] de Coninck, Bull. Acad. Roy. Belg., 1905, 94.
[2] de la Provostaye, Ann. Chim. Phys. (3), 5, 51. 1842.
[3] Kohn, Z. Anorg. Chem., 59, 111. 1908.

a fine crystalline mass which was very fluorescent. The spectrum of this was studied. The potassium, ammonium, lithium, and calcium salts were also prepared and seen to have characteristic line spectra, but were not studied further. The mineral autunite is a basic calcium uranyl phosphate which Stokes[1] says shows brilliant fluorescence, while chalcolite, the analagous copper compound, has none, but shows the same absorption bands characteristic of uranyl compounds.

CHROMATES.

An attempt was made to prepare the sodium uranyl chromate described by Rimbach, which resulted in a brown mass. The uranyl chromate UO_2CrO_4-$3H_2O$ (Orloff)[2] from UO_3 and CrO_3 gave yellow needles with no fluorescence. The potassium salt from $K_2Cr_2O_7$ and UO_3 was also without fluoresecence.

FLUORIDES.

Cragwall prepared the uranous and uranyl fluoride from U_3O_8 and HF, which showed practically no fluorescence. He also prepared the double potassium salt $K_3UO_2F_5$ by adding KF to uranyl nitrate and $(NH_4)_3\ UO_2F_5$ by dissolving $(NH_4)_2\ U_2O_7$ in HF.[3] The double salts showed characteristic spectra, but the fluorescence was very weak.

URANYL IODATE.

This salt was prepared from sodium iodate and uranyl nitrate by Cragwall by a method which, according to Artmann,[4] would result in $UO_2(IO_3)_2H_2O$ of the rhombic form. This showed little fluorescence.

MISCELLANEOUS INORGANIC COMPOUNDS.

An attempt was made to produce bromides and iodides analogous to the chloride salts without results, due to decomposition with the liberation of bromine and iodine. An attempt was also made to produce molybdyl and tungstyl ammonium chloride double salts analogous to the uranyl salts by heating the oxides with ammonium chloride and hydrochloric acid in sealed tubes, which in some cases resulted in crystals, which, however, showed no fluorescence. Uranic acid or H_2UO_4 was also sealed up in tubes with anhydrous liquid NH_3, CO_2, SO_2, and HCl. None of the resulting compounds were soluble or fluorescent, although changes took place, the carbonate being nearly white, the sulphur-dioxide tube greenish, due to reduction, and the ammonia tube reddish like the diuranate.

Of the uranates, the sodium potassium calcium and barium were made, none of which showed fluorescence, the first two being golden yellow plates, the latter two an amorphous greenish mass.

URANYL ACETATES.

The anhydrous uranyl acetate $UO_2(C_2H_3O_2)_2$ was prepared by Cragwall according to Spath[5] by adding acetic anhydride to uranic oxide. This latter took up some water and became partially the dihydrate. On recrystallizing some of the material from acetic-acid solution, small clear cubes were obtained which appeared to contain acetic acid of crystallization.

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[1] Stokes, Phil. Trans. Roy. Soc. London, 142, 518. 1852.
[2] Orloff, Chem. Ztg., 31, 375. 1907.
[3] H. F. Baker, Chem. Soc. Jour., 35, 763–769. 1879.
[4] Artmann, Z. Anorg. Chem., 79, 327, 1913.
[5] Spath, Monatsh. J. Ch. 33, 248. 1912.

Uranyl Acetate Dihydrate.

$UO_2(C_2H_3O_2)_2 2H_2O$.

This salt was prepared by Cragwall by recrystallizing the anhydride from water solution. There was also a stock of material from Kahlbaum and unknown sources. In an attempt to recrystallize this salt in large, clear crystals much difficulty was met, as it usually fills with cracks as it grows. The best material, having as much as 4 mm. cube of clear material, was obtained by supersaturating 2 grams in 200 c.c. and allowing a month or two to crystallize. The crystal properties were found to be similar to those described by Schabus,[1] the system being rhombic, with an axial ratio of 0.7817 : 1 : 0.3551, with the forms *m* (110), *a* (100), *r* (101), *n* (120), and *b* (010). The prism zone is very much striated, affording a continuous procession of reflections in the goniometer. Schabus finds cleavage on *m*, *a*, *b*, *c*, which accounts for their extreme friability. Zehenter[2] finds the specific gravity to be 2.893. The refractive index was determined through the dome as being 1.490 for light vibrating parallel to the *c* axis and 1.521 parallel to *b*.

The uranyl acetate trihydrate, which, according to Schabus, forms below 10° C., was not prepared. It crystallizes in the tetragonal system with an axial ratio of $a : c = 1 : 1.4054$.

DOUBLE URANYL ACETATES.

The sodium salt occurs in the acetates as well as the sulphates and is the only uranyl salt crystallizing in the regular system. The ammonium and potassium salts seem to be isomorphous, in spite of the fact that the potassium salt is said to contain 1 molecule of water and the ammonium salt to be anhydrous. The silver salt, which contains 1 molecule of water, is apparently isomorphous and the rubidium salt was found to have a similar axial ratio, as usual very near that of the ammonium salt. The similarity of axial ratio to that of the uranyl nitrate trihydrate suggests that these salts form a group that might well be studied further. The cæsium salt could not be obtained, the uranyl dihydrate crystallizing out and leaving the cæsium acetate in solution. The two hydrates of lithium uranyl acetate fully described by Wyrouboff[3] as being monoclinic were attempted, but only the room-temperature form was obtained. The double salts of uranyl acetate with bivalent acetates were in general prepared by dissolving the oxide or carbonate of the second metal in acetic acid in excess, adding uranyl acetate in calculated amount, with water enough for complete solution, and allowing to crystallize by slow evaporation. Difficulties were encountered in the preparation of some of the salts, such as the calcium salt, which Rammelsberg also could not obtain, as described by Weselsky,[4] which was finally prepared by Weselsky method of precipitation with calcium carbonate and solution of the precipitate in acetic acid. The barium salt was finally prepared by this method. The cadmium was never prepared at all; at least, no specimen that gave anything but the uranyl-acetate spectrum. An attempt to produce a mercuric acetate also failed.

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[1] Schabus, Prieschr. Wien, 207. 1855.
[2] Zehenter, Monats f. Ch., 21, 235. 1900.
[3] Wyrouboff, Bull. Soc. fran. min., 8, 115–122. 1885.
[4] Weselsky, J. Prakt. Chem., 75, 55. 1858.

The double acetates as a group were studied by Wertheim,[1] Schabus,[2] Grailich,[3] Weselsky,[4] and Rammelsberg.[5] The acetate group in general show much less intense fluorescence, tending to be of a dull yellow color.

The uranyl double acetates with bivalent metals may be divided into two classes—the normal and the abnormal. The group $HUO_2(C_2H_3O_2)_3 3H_2O$ appears to act as a unit in forming crystals. In the alkali double salts the water of crystallization seems to be lacking, at least in the well-confirmed cases of the sodium and ammonium salts. The case of the manganese, cadmium, and lead double salts seem also to be an exception, but with the other double acetates the ratio of uranium acetate to bivalent acetate seems to be 2 to 1. The water of crystallization is variously given from 7, which was found uniformly by Rammelsberg, to 8 by Wertheim and 10 by Grailich. Since the water is likely to run high, due to occluded mother-liquor, and is such a small per cent of the total weight, it is not unreasonable to assume that these really are all hexahydrates. The manganese, when satisfying this valence ratio, and magnesium salts seem also to have 2 molecules of water to each uranyl radical. In the case of the triple salts this requirement is exactly fulfilled, each valence of base having a $UO_2(C_2H_3O_2)3H_2O$ group attached to it.

In the case of the manganese, cadmium, and lead salts, this radical does not seem to act, but simply the two acetates are present in a 1 to 1 ratio. The spectra of the manganese salt was like that of the other double acetates; the cadmium was not formed or else gave a spectrum like that of the single acetate, and the lead was one of the salts which showed fluorescence lines coincident with spark lines, so that no generalization can be made.

Sodium Uranyl Acetate.

$NaUO_2(C_2H_3O_2)_3$.

This well-known salt described by Grailich[6] crystallizes in the regular system with the least or pentagonal dodecahedral symmetry. It is usually in the form of tetrahedra, yellow, with light green fluorescence. Johnsen[7] gives the specific gravity as 2.562 and the refractive index as 1.5014. Marback[8] and Traube[9] give the optical rotation as 1.48°. The best crystals, up to 3 mm. in thickness by 8 mm. diameter, were obtained on long standing of slightly supersaturated solutions. Dr. Nishikawa tried to obtain X-ray diffraction patterns with these crystals, but could obtain nothing.

Potassium Uranyl Acetate.

$KUO_2(C_2H_3O_2)_3H_2O$.

This salt was described by Wertheim[10] as having 1 molecule of water, which was also found by Schabus[11] and Rammelsberg.[12] A recent determination by

[1] Wertheim, Jour. of Prakt. Chem. 29, 207–231. 1843.
[2] Schabus, Best. d. Kystall gest. i. chem. Lab. Erz Prod. Preischr. Wien. 1855.
[3] Grailich, Kryst Opt. Untersuchung. Preisch. Wien, pp. 151–175. 1858.
[4] Weselsky, Jour. f. Prakt. Chem., 75, 55–62. 1858.
[5] Rammelsberg, Sitz. ber. Acad. Wiss. Berl., 857–887, 1884; Wied. Ann., 24, 293–318, 1885.
[6] Grailich, Preisschr. Wien, 151. 1858.
[7] Johnsen, N. Jahrbuch of Min. B. B., 23, 259. 1907.
[8] Marback, Pogg. Ann. d. Phys., 94, 422. 1855.
[9] Traube, Liebisch Grundries der Phys. Kryst., 327. 1896.
[10] Wertheim, J. Prakt. Chem. 29, 223. 1842.
[11] Schabus, Sitz. ber. k. Akad. Wiss Wien, 857. 1884.
[12] Rammelsberg, Wied. Ann., 24, 293. 1885.

Zehenter[1] gives 1/2 H_2O. Since the isomorphous ammonium salt is without water, and since both potassium acetate and uranyl acetate are hygroscopic and the salt occurs in needles, it seems likely that the water is not in the crystals. The crystals are mostly prism and pyramid of the tetragonal system, with the axial ratio $a:c = 1:1.2831$, according to Schabus. The specific gravity is given by Zehenter as 2.396. The best crystals were obtained by slow cooling, the tendency being to form needles. It was prepared by dissolving weighed potassium carbonate in an excess of acetic acid and adding the required amount of uranyl acetate.

Ammonium Uranyl Acetate.

$(NH_4)UO_2(C_2H_3O_2)_3$.

This salt was prepared and measured by Rammelsberg,[2] who found the axial ratio 1:1.4124 in the tetragonal system apparently isomorphous with the potassium salt. Grailich and Schrauf[3] assigned 1 molecule of water to this salt, but Rammelsberg denies this. Zehenter gives the specific gravity as 2.219. This was prepared by Cragwall by crystallizing equal molecular quantities of the two salts together.

Rubidium Uranyl Acetate.

$RbUO_2(C_2H_3O_2)_3.?H_2O$.

This salt was prepared by crystallizing uranyl acetate in calculated amount with rubidium acetate produced by evaporating off rubidium chloride several times with acetic acid. On cooling, tetragonal needles separated out, but on further evaporation the uranyl acetate separated, leaving the rubidium acetate in solution. The crystals were measured, giving an angle $o:m = (111):(110) = 26°33'$, which corresponds to an axial ratio of $a:c = 1:1.4151$.

Silver Uranyl Acetate.

$AgUO_2(C_2H_3O_2)_3H_2O$.

This salt was prepared and measured by Wertheim, who found it tetragonal, with an axial ratio of 1.5385. He assigns 1 molecule of water of crystallization, which seems doubtful. This was prepared from calculated quantities of uranyl acetate and silver acetate dissolved in aqueous acetic acid. If left in the light the solution decomposes, which resulted in many of the crystals being covered with a black coating of silver. These crystals are more inclined to be granular.

Lithium Uranyl Acetates.

$LiUO_2(C_2H_3O_2)_3 3H_2O$.

This is given by Wyrouboff[4] as crystallizing in the monoclinic system with the axial ratio $a:b:c = 1.2647:1:1.5849$; $\beta = 99°53'$. It forms readily on crystallization of water solution of the two acetates, but does not give very good crystals. The other hydrate, $LiUO_2(C_2H_3O_2)_3 5H_2O$, with forms below 15° was not obtained. The solution was made by adding to weighed lithium carbonate which had been treated with an excess of acetic acid a calculated amount of uranyl acetate. This was put in a desiccator over dehydrated potassium acetate in an unheated room in winter, but the $5H_2O$ phase was not found.

[1] Zehenter, Monatsh. f. Chem., 21, 235. 1900.
[2] Rammelsberg, Sitz. ber. Acad. Wiss. Berl. 1859.
[3] Schrauf, Sitz. ber. d. Acad. Wiss. Wien, 41, 779. 1860.
[4] Wyrouboff, Bull. Soc. fran. Min., 8, 115. 1885.

Magnesium Uranyl Acetates.

$Mg(UO_2.(C_2H_3O_2)_3)_27H_2O.$

This salt was found by Wertheim,[1] who assigned it 8 H_2O, examined by Grailich,[2] who gave $10H_2O$, and finally given $7H_2O$ by Rammelsberg.[3] It was found to crystallize in the rhombic system with the axial ratio 0.8944: 1: 0.9923, one of the series of five isomorphous salts Mg, Fe, Co, Ni, and Zn. Lang[4] gives negative double refraction, axes in (001) plane, bisectrix a $2E = 100°$, and $\rho < v$. This salt was prepared by evaporation of a solution made by adding to a weighed sample of MgO an excess of acetic acid and the calculated amount of uranyl acetate. The crystals grow fairly large, up to 5 mm. with some readiness.

$Mg(UO_2(C_2H_3O_2)_3)_212H_2O.$

This hydrate, according to Rammelsberg,[5] forms at low temperatures in large, rapidly weathering crystals with an axial ratio of 0.7667: 1: 0.5082. According to Grailich and Lang,[6] the double refraction is negative, the axes in a (100), bisectric c, $2E = 13°$ for red and 10.5° for blue. The fluorescence is given as very strong emerald green. This hydrate was not obtained for examination.

Calcium Uranyl Acetate.

$Ca(UO_2(C_2H_3O_2)_3)_28H_2O.$

The salt was prepared by Weselsky and examined by Grailich.[7] Rammelsberg attempted to repeat this determination and could not obtain good crystals. Grailich found them to be of the rhombic system, with an axial ratio of 0.9798:1: 0.3865, with many faces. Lang[8] found interior twins. Grailich found no pleochroism, but greenish-blue fluorescence. This salt was produced according to Weselsky's precipitation method after the addition method had failed.

Strontium Uranyl Acetate.

$Sr(UO_2(C_2H_3O_2)_3)_26?H_2O.$

This salt was also prepared by Weselsky and could not be obtained by Rammelsberg. It was measured by Grailich, who reports it as being in the tetragonal system, with an axial ratio of 1: 0.3887. No trouble was found in producing it from strontium carbonate, acetic acid, and uranyl acetate.

Barium Uranyl Acetate.

$Ba(UO_2(C_2H_3O_2)_3)_26H_2O.$

This salt was first produced by Wertheim and[9] later described by Rammelsberg,[10] both of whom found 6 molecules of water, but neither of whom obtained crystals good enough to measure. The Weselsky method was also necessary to produce this compound, the first attempt giving only the uranyl acetate crystals.

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[1] Wertheim, *l. c.*, 225.
[2] Grailich, *l. c.*, 152.
[3] Rammelsberg, Wied. Ann., 24, 303.
[4] Lang, *l. c.*, 107.
[5] Rammelsberg, Sitz. ber., 869.
[6] Lang, Sitz. ber d. Akad. Wiss Wien, 108, IIa, 562. 1899.
[7] Grailich, *l. c.*, 159.
[8] Lang, *l. c.*, 107.
[9] Wertheim, *l. c.*, 230.
[10] Rammelsberg, *l. c.*, 300.

Zinc Uranyl Acetate.

$$Zn\,(UO_2(C_2H_3O_2)_3)_2\,7H_2O.$$

This salt was prepared by Weselsky[1] and examined by Grailich.[2] Rammelsberg found the axial ratio to be 0.8749 : 1 : 0.9493 in the rhombic system. Grailich and Lang[3] found negative double refraction with the axes in c (001), bisectrix b. The color, according to Grailich, is yellow with weak pleochroism; fluorescence is faint greenish. This salt from zinc oxide, acetic acid, and uranyl acetate crystallized after some trouble in rhombic plates with little fluorescence. The uranyl acetate sometimes separated without the formation of the double salt. This belongs to the isomorphous magnesium group.

Cadmium Uranyl Acetate.

$$Cd.UO_2.(C_2H_3O_2)_4 6H_2O.$$

These crystals were made by Weselsky[4] and examined by Grailich, who found an axial ratio of 0.6289 : 1 : 0.3904 in the rhombic system. These crystals were also analyzed by Rammelsberg,[5] who found that the composition did not correspond to that of the zinc salt, but had a 1 to 1 ratio of bivalent cadmium to uranium, thus making it like manganese and lead. These crystals could not be prepared, nothing but the uranyl acetate spectra being obtained.

Manganese Uranyl Acetate.

$$MnUO_2(C_2H_3O_2)_4 6H_2O.$$

These crystals, prepared by Weselsky[6] and examined by Grailich,[7] were found to have the axial ratio of 0.6330 : 1 : 0.3942 in the rhombic system by Rammelsberg. The optical properties, according to Lang, are double refraction, negative, plane of the axes a (100), bisectric c, $2E = 31°$, with a yellow color. When prepared by evaporation of an acetic-acid solution of manganese carbonate and uranyl acetate, small yellow crystals were obtained.

$$Mn\,[(UO_2)\,(C_2H_3O_2)_3]_2\,12H_2O.$$

These efflorescing crystals, obtained by Rammelsberg[8] from the 1 : 1 solution of the acetates while warm, which solution later deposited the other hydrate, is isomorphous with the magnesium dodecahydrate. Rammelsberg found it to be of the rhombic system, with the axial ratio of 0.7536 : 1 : 0.4957.

Lead Uranyl Acetate.

$$PbUO_2(C_2H_3O_2)_4 4H_2O.$$

This salt was obtained by Wertheim[9] and later by Rammelsberg,[10] who gave it the above formula, which puts it in the 1 : 1 class with cadmium and manganese. The crystals are very readily formed as needles of any length—the greater the supersaturation the longer the needles. Some fairly compact plates were obtained as a second crop from a highly supersaturated solution. These were made from lead acetate and uranyl acetate in weighed proportions.

TRIPLE ACETATES.

These salts were discovered by Rammelsberg[11] in an attempt to get a copper uranyl double acetate and are found when sodium acetate is present with the bivalent metals, magnesium, manganese, iron, nickel, cobalt, copper, zinc,

[1] Weselsky, . *lc.*, 58.
[2] Grailich, *l. c.*, 171.
[3] Lang, *l. c.*, 51.
[4] Weselsky, *l. c.*,61.
[5] Rammelsberg, *l. c.*, 887.
[6] Weselsky, *l. c.*, 59.
[7] Grailich, *l. c.*, 175.
[8] Rammelsberg, *l. c.*, 872.
[9] Wertheim, *l. c.*, 227.
[10] Rammelsberg, Wied. Ann., 314.
[11] *Ibid.*, 315.

and cadmium salts being reported. They are characterized by a temperature dimorphism being above a given temperature, trigonal, and below that monoclinic twins and pseudotrigonal. They all have the same type formula derived from the monovalent uraniacetic acid $HUO_2(C_2H_3O_2)_3 3H_2O$, which takes on in this case 1 atom each of monovalent metal (sodium in all cases studied) and 1 bivalent metal. These formula may also be written $NaOH+R(OH)_2+3UO_2(OH)_2 + 9HC_2H_3O_2$, which would explain the exact relation between the number of acetic radicals and molecules of water of crystallization. This series was studied by Erb[1] and by Wyrouboff.[2] The temperature change was studied by Schwarz.[3] This group is characterized by the pseudotrigonal appearance of a large basal pinacoid, six-sided, due to rhombohedron faces which are uneven, due to twinning. They are readily distinguished from uranyl acetate or the metallic acetate or uranyl double acetates by this characteristic shape. They do, however, resemble the sodium uranyl acetate considerably if it has uneven faces, due to the varying composition of the solution as it crystallizes. Under the crossed nicols, however, there is no question, the very characteristic twinning surfaces showing unmistakably.

Sodium Magnesium Uranyl Acetate.

$NaMg[(UO_2(C_2H_3O_2)_3\ 3H_2O_2]_3$.

These crystals, according to Wyrouboff,[4] are simply monoclinic if grown below 15° C., but as the temperature rises the twins become more numerous, until at 50° the whole crystal becomes trigonal. This process then reverses on cooling. Erb[5] describes them as sulphur-yellow crystals which weather readily. The axial ratio has not been determined closely because of the twinning. These crystals were grown better by slow evaporation than by slow or rapid cooling of supersaturated solutions.

Sodium Zinc Uranyl Acetate.

$NaZn[(UO_2(C_2H_3O_2)\ 3H_2O]_3$.

These crystals were produced by Erb, who did not obtain sufficient measurements to calculate the axial ratio. The temperature of conversion was found by Schwarz to be 95°. These crystals were made by adding to zinc oxide an excess of acetic acid, sodium uranyl acetate, and uranyl acetate in calculated proportions. These crystals were identified by the twins, as shown by polarization. They were found to weather fairly rapidly, even in moist summer weather.

Sodium Cadmium Uranyl Acetate.

$NaCa[UO_2(C_2H_3O_2)_3\ 3H_2O]_3$.

These crystals, prepared and measured by Wyrouboff,[6] have the axial ratio $a:b:c=0.5162:1:0.9798$; $\beta=90°9'$; plane of the axes normal to b (010) and nearly parallel to a (100); positive bisectrix parallel to b, with large axial angle. The change to a uniaxial figure does not take place until nearly 200°, at which temperature the crystals effloresce.

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[1] Erb, N. Jahr. of Min. B. B., 6, 121–147. 1888–89.
[2] Wyrouboff, Bull. Soc. fran. Min. 24, 93–104. 1901.
[3] Schwarz, Beitr. Z. Kenntn. d. umkehrbaren Umwandlungen polymorpher Korper. Preisschr d. Univ. Gottingen. 1892.
[4] Wyrouboff, *l. c.*, 104.
[5] Erb, *l. c.*, 126.
[6] Wyrouboff, *l. c.*, 103.

Sodium Copper Uranyl Acetate.

$Na\ Cu[UO_2(C_2H_3O_2)_3\ 3H_2O]_3$.

This was the first salt of this series to be discovered by Rammelsberg. The axial ratio is given by Wyrouboff as $a:b:c=0.5354:1:0.9950$; $\beta=89°\ 55'$. The double refraction is weakly positive, plane of the axes normal to b (010); the bisectrix 50° from c axis in the acute angle through the face c (001); $2E = 90°\ 50'$; dispersion weak, $r < v$. According to Wyrouboff, it only becomes uniaxial at 140°, while Schwarz finds the conversion-point at 93.8°. This salt was prepared from cupric hydroxide, acetic acid, uranyl acetate, and sodium acetate in weighed amounts. On slow evaporation, large, clear crystals, though not free from twins, were obtained, some being 1 cm. in diameter and 2 mm. thick. These were sealed in glass to prevent efflorescence.

An attempt was made to produce the cobalt salt of this group, but it was not very successful. The manganese, iron, and nickel were not tried. The last salt was studied rather completely by Johnsen[1] in an investigation of twinning.

Uranyl Oxalate.

$UO_2(C_2O_4)\ 3H_2O$.

This salt was described by Peligot and Ebelmen[2] and later by Zimmerman.[3] This is an apparently amorphous powder produced by adding oxalic acid to the neutral nitrate, which shows under the microscope small grains with brilliant polarization colors and an extinction angle with the long side of the crystals of 13°. A specimen of this was prepared by Cragwall and some material was also purified this way.

DOUBLE URANYL OXALATE.

The double salts seem to be formed fairly readily, the potassium salt being described by Ebelmen[4] and the ammonium salt by de la Provostage[5] and by Rammelsberg.[6] Wyrouboff[7] makes a comprehensive review, giving the following:

$K_2\ UO_2(C_2O_4)_2\ 3H_2O$ monoclinic.
$(NH_4)_2\ UO_2(C_2O_4)_2\ 2H_2O$ rhombic.
$Cs_2\ UO_2(C_2O_4)_2\ 2H_2O$ rhombic isomorphous with above.
$Tl_2\ UO_2(C_2O_4)_2\ 2H_2O$ rhombic isomorphous with above.
$Na_2\ UO_2\ (C_2O_4)_2\ 6H_2O$ triclinic.
$(NH_4)_4\ UO_2\ (C_2O_4)_3$ monoclinic.
$Tl_4\ UO_2\ (C_2O_4)_3$ monoclinic isomorphous with above.
$K_6\ UO_2\ (C_2O_4)_4\ 10H_2O$ triclinic.

None of these salts were tried.

Uranyl Tartrate.

$UO_2C_4H_4O_6.4H_2O$.

This salt was prepared by Cragwall by the method of Peligot[8] from uranyl hydroxide $UO_2(OH)_2$ from the ignition of uranyl nitrate and tartaric acid.

[1] Johnsen, N. Jahrb. Min. B. B., 23, 259. 1907.
[2] Peligot and Ebelmen, Liebig. Ann. Chem. 43, 282, 287. 1842.
[3] Zimmerman, Liebig. Ann. Chem., 232, 300. 1886.
[4] Ebelmen, Ann. Chim. Phys. (3), 5, 200. 1842.
[5] de la Provostage, *ibid.*, 49.
[6] Rammelsberg, Handbuch d. Krystall. Chem., 264. 1855.
[7] Wyrouboff, Bull. Soc. Fran. Min., 32, 352. 1909.
[8] Peligot, Liebig Ann. Chem., 56, 231. 1845.

This was recrystallized from water and left microscopic plates with wide black edges, as on a crystal lying on *b* (010) and bounded by *m* (110) and *c* (001), or else having a very high index, a low double refraction, and straight hyperbolas, as from a tipped uniaxial crystal or near an optic axis.

DOUBLE URANYL TARTRATES.

The tartrates are exceedingly soluble, and likely to result in gums on drying, which do not crystallize. The existence of a sodium double salt in solution is indicated by the work of Grossman[1] and Loeb on the effect of heavy metals on the rotation of tartaric acid. The potassium double salt is described by Frisch[2] and the antimonyl salt by Peligot (see uranyl tartrate), but none of the salts show fluorescence, so they were not taken up further. The corresponding molybdyl and tungstyl compounds were attempted, since the oxides are soluble in tartaric acid, but only thick gums which did not crystallize or fluoresce were obtained.

Potassium Uranyl Tartrate.

$K_2UO_2(C_4H_4O_6)_2$.

This salt, described by Frisch, was prepared by Cragwall by adding uranyl nitrate to potassium tartrate and washing free from nitrates. Since Frisch produced his material by dissolving precipitated uranyl hydroxide in acid potassium tartrate (Weinstein) and found that it could not be crystallized by drying, but was precipitated by alcohol, it seems probable that the material which Cragwall obtained on washing was simply the acid potassium tartrate itself. Examination for fluorescence and under the microscope indicated this.

Antimonyl Uranyl Tartrate.

$UO_2.(SbO.C_4H_4O_6)_2\ 4H_2O$.

This is produced, according to Peligot, by adding uranyl nitrate solution to potassium antimonyl tartrate solution. Cragwall washed the precipitate free from nitrates. The resulting material appeared to be amorphous and showed no fluorescence. In this case both basic radicals are commonly in the complex anion, so that it is difficult to decide which comes first.

Potassium Uranyl Propionate.

$K\ UO_2(C_2H_5O_2)_3$.

Rimbach[3] examined the potassium and ammonium double salts with propionic acid and the potassium double salt with butyric and valerianic acids. These crystallize in tetrahedra, according to Sachs,[4] but were not attempted for this work.

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[1] Grossman and Loeb, Z. Phys. Chem., 72, 93. 1910.
[2] Frisch, J. Prakt. Chem. 97, 281. 1866.
[3] Rimbach, Ber., 37, 484. 1904.
[4] Sachs, Ber. 37, 484. 1904.

APPENDIX 2.

ON PHOSPHOROSCOPES.

The uranium salts have exhibited under photo-excitation a type of phosphorescence which persists but a few thousandths of a second, while under cathodo-excitation the type endures for several minutes. It was necessary to devise two phosphoroscopes of entirely different design to measure the two types of phosphorescence. The choice of a suitable phosphoroscope is a matter of great importance; hence, a brief summary of the types of phosphoroscopes which have been employed since the time of the great pioneer student of phosphorescence, E. Becquerel, follows. Among the considerations which present themselves when the construction of a phosphoroscope is contemplated are the quantity of phosphorescent material available, the total time of decay, the temperature at which the specimen is to be studied, the nature of the excitation (*e. g.*; photo-, ultra-violet, cathode rays, etc.), the ease with which saturation is obtained, and the initial brightness of the specimen. The phosphoroscopes which have been constructed can be divided into three classes:

Type 1.—The specimen is periodically excited and periodically viewed at a later phase.

Type 2.—The specimen is continuously excited and continuously viewed at a later phase.

Type 3.—The specimen is excited for a measured interval of time and the intensity measured at a later time. This method is applicable to the slowest types of decay.

Machines which may be classified as belonging to type 1 must operate at such speeds that no flicker is noticeable; hence the weakest intensity measured must fall within a total time of decay of one-sixteenth of a second. Many natural crystals, under photo-excitation, present very interesting phosphorescence processes which apparently cease in less than this time. The very first steps in the long-time decays of such substances as the natural and artificial sulphides may be studied with the aid of a phosphoroscope belonging to type 1. E. Becquerel[1] devised, among other forms, a phosphoroscope of the intermittently excited type. The specimen was mounted between two parallel disks and was alternately illuminated and observed through properly adjusted openings in the disks. Figure 1 shows two such disks, each having four open sectors, mounted on the same axis but in different phase. Becquerel caused the exciting light to pass into the translucent crystal through

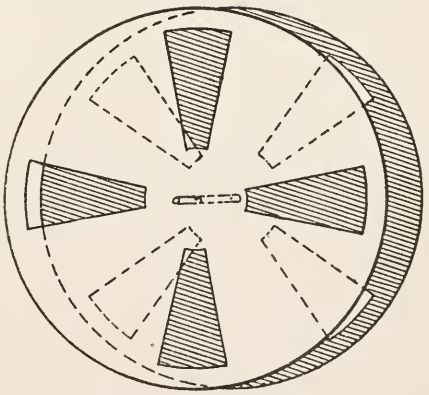

FIG. 1.

[1] E. Becquerel, Annales de Chimie et de Physique (3), 55, p. 5. 1859.

the rear disk, while the opaque sector prevented the light from coming through the phosphoroscope to the eye. As the disk was revolving at a high speed, the light was quickly stopped from passing to the crystal by the interposition of an opaque sector of the rear disk. A small fraction of a second later the continued rotation brought an open sector of the front disk in line with the crystal and the eye, thereby allowing the phosphorescent light to be viewed on a dark field. The rotating parts were neatly mounted in a brass drum and driven by a crank through a system of gears. With such a type of phosphoroscope Becquerel detected the glow of the platino-cyanides only 0.003 of a second after excitation.

It is evident that to view opaque specimens, the excitation can not be directly behind the specimen; hence Becquerel[1] devised a phosphoroscope possessing only one rotating disk, figure 2, both diagrams with three openings, *K*, *L*, and *R*, arranged 120° apart. The disk revolved on a vertical axis between two fixed openings, 180° apart, the exciting light from *X* passing in through one of these two openings and the luminescent light passing out from the specimen *P*, upper diagram, through the other opening to the observer *O* a fraction of a second later. In figure 2 the sector is shown, in elevation, at such a position that the open sector *R* admits exciting light to *P*, and it is evident that an opaque sector is at that time to be found at *S*. On the other hand, when *S* is opened by the passage of an open sector, the open sector *R* has passed out of the line *XP* and an opaque sector is interposed.

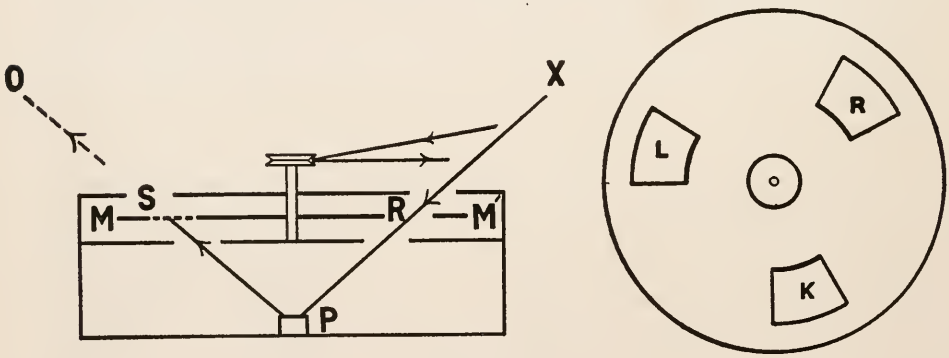

FIG. 2.

E. Wiedmann[2] devised a phosphoroscope consisting essentially of a hollow brass drum fitted with a collimator and lens and revolving disk for the admission of the exciting light. The exciting light passed intermittently through the open sectors of a sectored disk and the specimen, which was mounted within the drum, was thus intermittently excited. For the purpose of viewing opaque specimens and liquids at a later phase, the revolving disk carried on the periphery a band with open sectors for excitation; thus the path of the phosphorescent light was at right angles to that of the exciting light. Wiedemann constructed driving-gears with a ratio of 1,000 : 1 and hence obtained a rotary speed as great as 140 revolutions per second. Either the unassisted eye or a spectrometer was employed to view the phosphorescence. Stray

[1] E. Becquerel, Annales de Chimie et de Physique (3), v. 55, p. 80. 1859.
[2] E. Wiedmann, Wiedmann's Annalen, vol. 34, p. 446. 1888.

ight, always a menace in phosphorescent studies where photo-excitation is used, was present, and Wiedemann appreciated the necessity of devising some addition to his apparatus for the purpose of eliminating it. He favored the addition of another revolving sector, similar to and coaxial with the first, having openings in phase with it, and mounted between the first sector and the lens. When it is considered that the intensity of the undispersed phosphorescence is from 1/100 to 1/1,000,000 that of the exciting light, it is evident that the introduction of a small per cent of the exciting light into the field of the phosphorescence completely aborts any attempt at quantitative measurements.

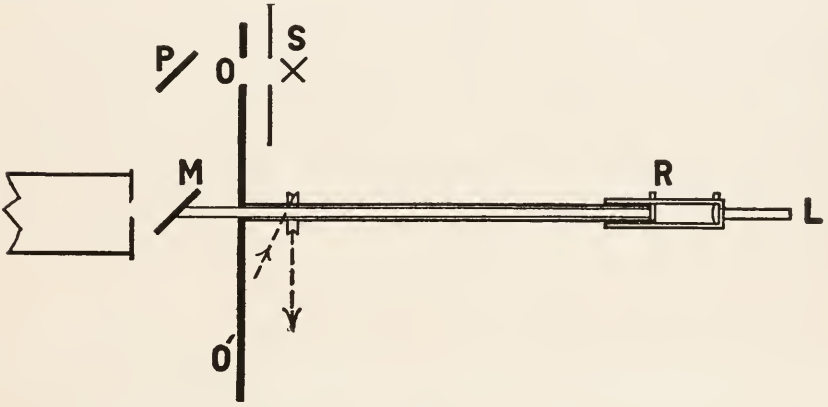

FIG. 3.

E. Merritt[1] devised a phosphoroscope of the first type in which the phosphorescent surface P (see fig. 3) was illuminated periodically by the passage of light from a spark S through an opening through a revolving disk OO'. The phosphorescence could be observed at the desired later time by changing the phase, while the machine is turning, of the mirror M relative to the opening O. This was accomplished in a unique manner by means of the rod L, which engages a hollow sleeve R having a spiral slot cut in it. A pin capable of sliding in this slot and attached to the opposite end of the same inner shaft as the mirror M, is moved into different phases with the disk OO', which is mounted on the outside shaft. This outer shaft is driven by a belt and pulley and is keyed to the sleeve R; thus the drive is complete. Rod L does not rotate, but can be locked at any desired phase. Reflection of the phosphorescence, then, occurs at M, a simple photometer being employed to view the light. On the revolving shaft was mounted a worm-gear for recording the number of revolutions per minute. With this form of phosphoroscope the curves of decay of many substances were traced from zero time up to 0.06 second.

In the preceding phosphoroscopes the source of light has not been intermittent, but the periodic interruption of the beam of exciting light has produced the effect of intermittent excitation on the specimen. Another group of instruments belonging to this type employs an intermittent discharge from condenser, induction coil, or transformer, as in the spark phosphoroscope of

[1] E. Merritt, Nichols and Merritt, Studies in Luminescence, Carnegie Inst. Wash. Pub. No. 152, p. 109. 1912.

Laborde,[1] which included a rotating pattern to hide the specimen from the observer during excitation by the spark from an induction coil, and later uncover the specimen.

Wm. Crookes,[2] in his study of the cathode phosphorescence of yttria, noted that the color at the beginning of decay was different from that observed after the decay had continued for a short period, and accordingly devised a phosphoroscope to study this change. Figure 4 serves to show that it was of the sectored-disk form and driven by cord and pulley. At a convenient distance was located an induction coil whose primary circuit was alternately made and broken by a commutator near the end of the revolving shaft *C*. The brushes could be so shifted as to cause the excitation of the phosphorescent substance *P* when an opaque sector passed between *P* and the eye. It was possible to change the period of decay by changing the speed or by changing the phase of the brushes relative to the edge of the sector. The phosphorescent substance was mounted in a convenient form of cathode-ray tube and excited by the discharge from the secondary of the coil. With the aid of the spectrometer, Crookes discovered that different lines appeared in the spectrum of the phosphorescent yttrium after 0.000875 second than at 0.0035 second.

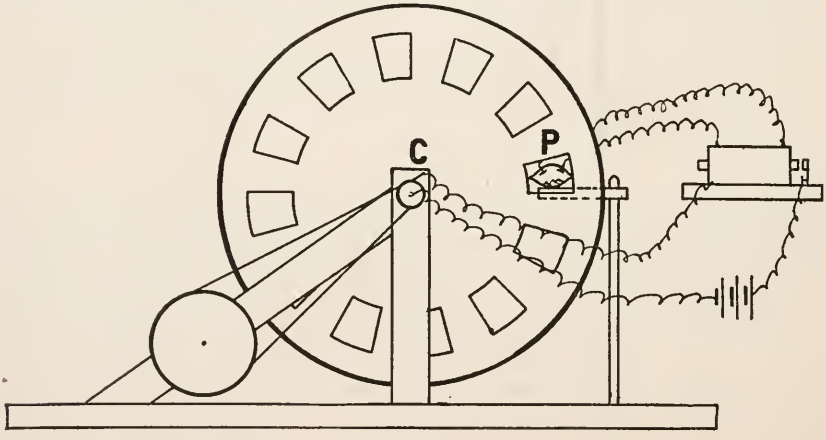

FIG. 4.

Ph. Lenard[3] devised a phosphoroscope which differs from the preceding forms, since no revolving disk is employed. To hide the specimen from view during excitation he used the motion of a screen mounted on the plunger of a Ruhmkorff mercury interrupter. The frequency of the interrupter was determined by that of the spring fork on which it was balanced; hence change in the period between excitation and observation was accomplished by changing forks. The discharge of a condenser in parallel with secondary circuit of the coil was thus timed by the interruptions of the primary circuit to occur while the vibrating screen was in front of the specimen.

De Watteville[4] constructed a machine similar in principle to that of Laborde and Crookes (see fig. 5). The specimen, together with the spark, was mounted

[1] Laborde, Comptes Rendus, vol. 68, p. 1576.
[2] Crookes, Proceedings of the Royal Society, vol. 42, p. 111. 1887.
[3] Ph. Lenard, Wiedmann's Annalen, 46, p. 637.
[4] De Watteville, Comptes Rendus, 142, p. 1078.

in the box K and was visible to the observer, except when the two arms of the rotating disk D intercepted the phosphorescent light. At such times one of the points, P or P', completed the circuit from B through A to K, allowing the discharge of the condenser C to excite the specimen at K; the condenser had been previously charged by coil S. Twice a revolution, then, the specimen was excited and observed.

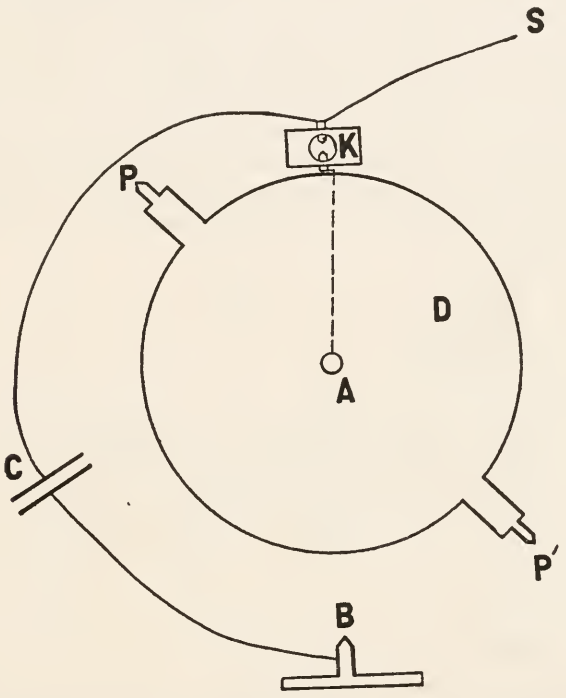

FIG. 5.

Nichols and Howes,[1] to study the phosphorescence of the uranyl salts, devised a phosphoroscope of considerable precision. Except for the work of Nichols and Merritt, Trowbridge, Ives, and a few others, the previously mentioned students of phosphorescence have been content to measure the intensity at two or three periods of decay, but the above-mentioned investigators have taken many observations on one substance and established curves of decay for each substance studied. For such measurements, refinements for precluding measureable stray light and for accurately measuring the time intervals and for maintaining constant speed are a necessity. The synchronophosphorosope (see fig. 6) was so named because it employs the principle of a sectored disk mounted on the axle of a synchronous motor $A.\ C.$ This motor was raised to synchronous speed by the direct-current motor $D.\ C.$ The transformer TT was attached to the same alternating-current terminals as was the $A.\ C.$ motor; hence the discharge of the condenser occurred as many times per second as the number of wave-crests, *i. e.*, 120. There were four opaque sectors and four open sectors in the disk WW, and since the four-pole machine turned at a speed of 30 revolutions per second, there were 120 eclipses

[1] Nichols and Howes, Science, n. s., vol. 43, p. 937. 1916.

per second. By means of a small set-screw the disk could be clamped at various positions on the shaft, corresponding to various times in the decay process. Without the star-wheel *SS* the discharge of the condenser *KK* produced an exciting spark at *E*, which, with the aid of a revolving mirror, was found to consist of a pilot-spark, followed by five or six smaller sparks; hence the zinc star-wheel *SS* was mounted on the shaft to reduce the discharge to one spark. By experimenting with small and large capacities it was found that resonance must be recognized, and the proper amount of capacity to produce a regular, strong spark was finally discovered. The measurements of time were read with the aid of the light yielded by the exciting spark by noting the position of the edge of the sectors on a protractor mounted rigidly in front of the machine. The range of times accurately measureable include those from 0.0001 to 0.0040 second by 0.0001-second steps. The photometer, spectro-photometer, camera, and spectrograph have been successfully used with this instrument.

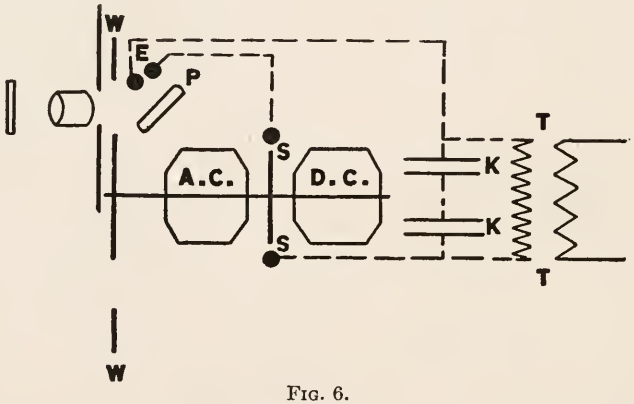

FIG. 6.

In their preliminary study of the cathodo-phosphorescence of the rare earths, Nichols, Wick, and Wilber[1] employed a phosphoroscope with a disk mounted on the shaft of a motor. The primary of an induction coil was interrupted by a plunger attached to a crank on the shaft of the motor. The plunger, once in a revolution, dipped into the mercury cistern, while the opaque portion of the disk hid the specimen from view, and as a result the specimen was excited by the discharge of the secondary coil through a cathode-ray tube, much after the manner of Crookes's device.

The change in time between excitation and observation was accomplished by changing the speed of the motor, and an ammeter in the field circuit was calibrated to measure the angular velocity. It is evident that with only one excitation per revolution only one open sector could be used.

The second type of phosphoroscope includes those instruments by means of which the specimen is constantly excited and constantly viewed at a later time. Such a form had its origin with E. Becquerel.[2] This form was used for lecture demonstrations by Tyndall.[3] In its simplest form it consists of a

[1] Nichols, Wick, and Wilber, Physical Review (2), vol. 14, 1919.
[2] Becquerel, E., Annales de Chimie et de Physique (3), vol. 62, p. 5. 1861.
[3] Tyndall, see Lewis Wright, "Light," p. 152. London, 1882.

drum (see fig. 7) whose periphery P is covered with a phosphorescent substance, provided with a source of excitation S mounted in a box A, and driven by belt BB and pulley. The viewing collimator or photometer is indicated at E.

Kester[1] employed a device of this type, together with spectrometers and radiometer, to study the relation of intensity of excitation to that of phosphorescence.

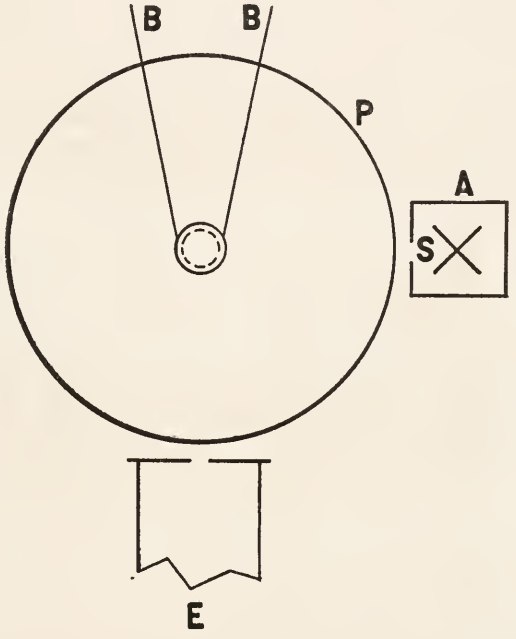

FIG. 7.

Waggoner[2] mounted on a vertical shaft an iron drum 45 cm. in diameter. This mass, being considerable, acted as a balance on the irregularities of the motor speed. The exciting spark was so mounted that it could be moved about the drum, thus enabling the observer to measure the brightness at various times after the spark ceased. The periphery was painted, as before, with the phosphorescent substance. The revolutions of the drum were automatically recorded on a chronograph. With this device the spectrum of early phosphorescence was studied with the aid of the spectrometer and decay curves of the total visible radiation were taken.

Nichols and Howes,[3] in the study of the phosphorescence of calcite, employed this type with a drum of 8.0 cm. diameter (see fig. 8). The eye-piece E was arranged at 180° from the spark A, the spark thus being completely hidden from the observer by the opaque drum D. Effective screening was added to prevent stray light from entering either face of the Lummer-Brodhun cube L. B. and a filter F was interposed between the comparison lamp C

[1] Kester, Physical Review (1), vol. 9, p. 164.
[2] Waggoner, Carnegie Inst. Wash. Pub. No. 152, p. 119.
[3] Nichols, Howes, and Wilber, Physical Review (2), vol. 12, p. 350. 1918.

and the cube to produce a color match with the reddish color of the phosphorescence. Although the angle between spark and observing photometer remained constantly 180°, the time of decay could be varied between 0.01 second and 3 or 4 seconds by changing the motor field or by throwing in a

DISK PHOSPHOROSCOPE.

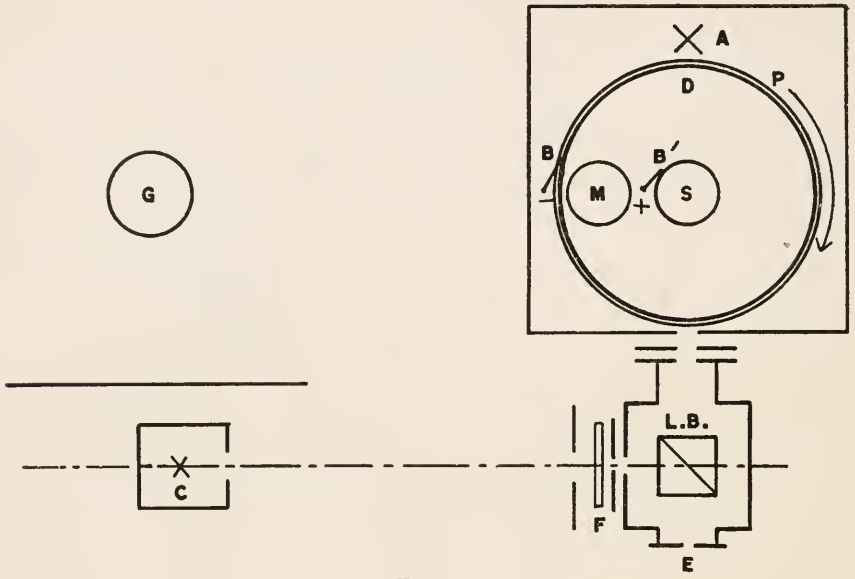

FIG. 8.

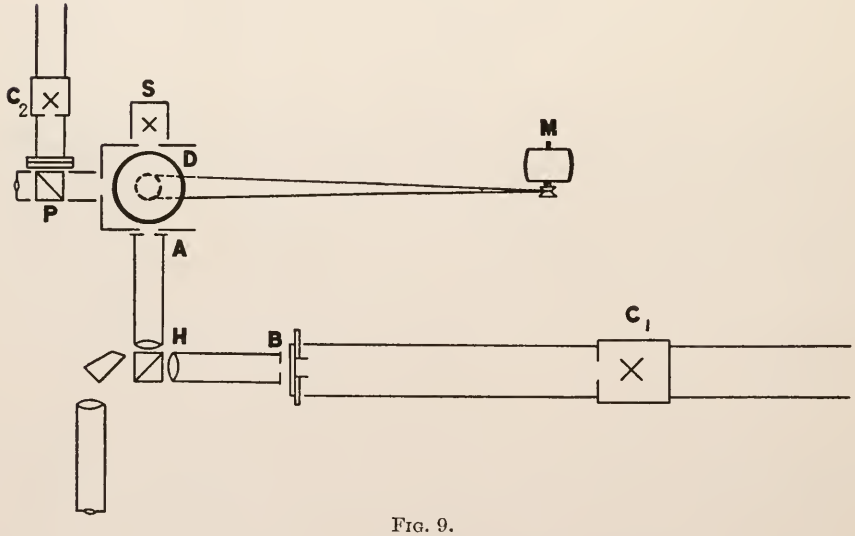

FIG. 9.

worm-gear drive. Two features were added to make the device more useful. First, the phosphorescent substance was never painted on the disk, but on brass rings which fitted neatly on the disk; second, the speeds were known by reading on a galvanometer *G* the deflections produced by a current induced

by a disk below the phosphorescent disk, but on the same shaft. This disk cut the field between two electromagnets M, one brush B on the rim, the other, B', on the shaft delivering the current to the galvanometer. The constancy of the magnetic field was maintained by examining the readings of an ammeter in series with the electromagnets and storage cells, and precautions were taken to eliminate thermal electromotive forces at the brushes. In the use of this type of phosphoroscope, as well as the first type, readings of in-

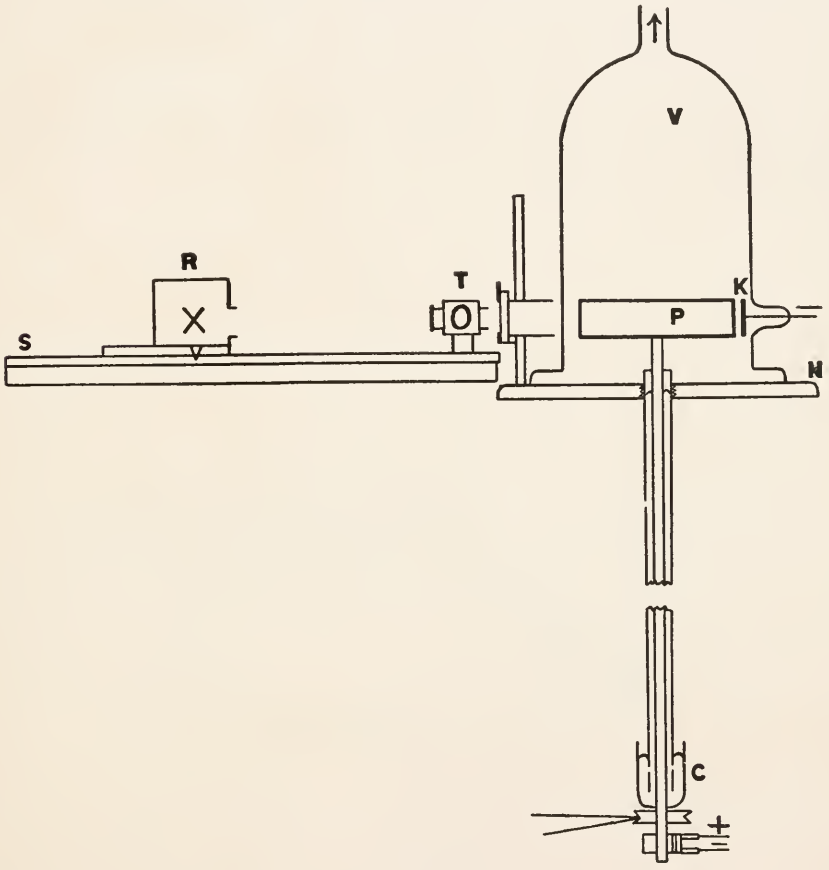

FIG. 10.

tensity are only comparable through a range of speeds for which saturation is obtained. With the red variety of calcite, saturation was found to exist with the iron spark 1 cm. from the disk for all speeds, which gave more than 0.02 second decay; hence measurements in which the time interval from the close of excitation to observation was not greater than 0.02 second were rejected. To use this instrument with greater precision it is necessary to take account of the variations in the spark. For this purpose an auxiliary station, with photometer P and lamp C_2, was arranged (fig. 9), where simultaneous readings of intensity of phosphorescence were taken while the chief observer, with aid of the spectrophotometer H and lamp C_1, measured the intensity of the phosphorescence throughout the spectrum.

To study the early stages of the cathodo-phosphorescence of calcite, Nichols and Howes[1] devised a vacuum phosphoroscope, outlined in figure 10. The phosphorescent specimen was applied to the periphery of the disk P and excited by means of the cathode discharge from K. The vacuum-tube V was fitted to the ground plate N. The shaft was balanced in an iron tube 115 cm. in length, the mercury rising from the iron reservoir C to the barometric height. The shaft was driven by a pulley, cord, and variable-speed motor, and the revolutions were recorded by the commutating device at the bottom wired to the chronograph. Intensities of phosphorescence were measured with the aid of lamp P, photometer bar S, and Lummer-Brodhun cube T.

The third type of phosphoroscope, in which the specimen is excited for a definite time and viewed at varying but definite times after excitation, includes the form used by Nichols and Merritt in their extensive studies[2] of the luminescence of sidot blende.

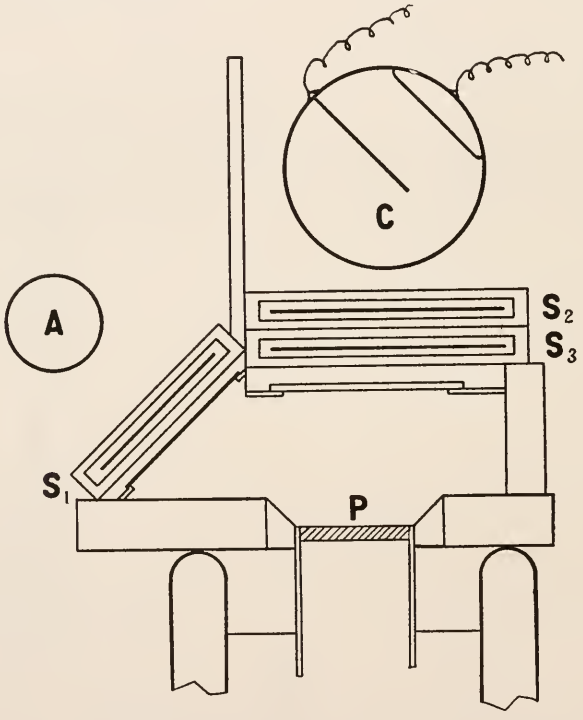

Fig. 11.

The specimen was mounted diagonally in a box having two openings with shutters, one to admit excitation, the other to allow the luminescence to be viewed after excitation. The eye of the observer was thus protected from the brilliant luminescence during excitation, but was able to view the phosphorescence with no fatigue when the shutter of the luminescence window opened. The time when the phosphorescence intensity became equal to that of the comparison field was recorded on the chronograph by means of a key in the

[1] Nichols, Howes, and Wilber, *l. c.*
[2] Nichols and Merritt, Carnegie Inst. Wash. Pub. No. 152, p. 41.

hand of the observer. A series of such comparisons, together with the initial time, formed a series of points for a decay curve. It is clear that such a device is only suitable for the study of decay which endures for several minutes.

E. H. Kennard[1] devised a phosphoroscope of this type with shutters actuated by the magnetic release of phosphor-bronze springs. Three shutters (S_1, S_2, S_3, of fig. 11) were used, S_1 to admit exciting light from the mercury arc A to the specimen P, S_2 and S_3 to limit the time during which the phosphorescence was allowed to produce photo-electric action on the cell C. The latter adaptation to phosphorescence work is unique. In his preliminary work the times between opening and closing of shutters were determined from the known curve of a ballistic galvanometer, the passage of a shutter opening and closing shunts which allowed a definite quantity of electricity to pass into the galvanometer. In his later work the shutters were magnetically released by the swing of a seconds pendulum across mercury cups set at convenient positions along the path of the bob. The photo-electric current, for low intensities, is proportional to the intensity of phosphorescence and was measured by a quadrant electrometer.

It is to be inferred from the preceding summary on phosphoroscopes that there may be no single machine which is well adapted to the study of a particular phosphorescent specimen under investigation. As in the study of phosphorescence in the past, the investigator has often devised one or more machines for the study of the various types of phosphorescence; so in the future the machine must be adapted to the behavior of the specimen. Then, too, the precision with which the time of observation is desired makes it necessary that the modern phosphoroscope be equipped with an accurate and if possible a direct-reading speed register. The plotting of decay curves by Nichols and Merritt, Trowbridge, Ives, and others made it imperative that both times and excitations be well known. The lack of constancy of excitation has been recognized and observations corrected. The importance of obtaining the same degree of saturation before decay begins is paramount if results are to be considered comparable. In the use of the continuously excited type the importance of this factor becomes evident. The use of the interrupted excitation type for eclipses of 16 or less a second should be entirely avoided, because of the behavior of the eye when flicker is noticeable. The human eye should not be fatigued beyond instant recovery during the process of observing decay, neither should it be dark-adapted before beginning a set of observations. The necessity of adequate screening is of great importance when it is considered that luminescence radiation is several thousand times less than the photo-excitation of approximately the same wave-length. Stray luminescence may add to the selected portion of the luminescence beam and produce errors. These factors are fundamental considerations for the future student of phosphorescence.

[1] Kennard, Physical Review (2), vol. 4, p. 278. 1914.

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